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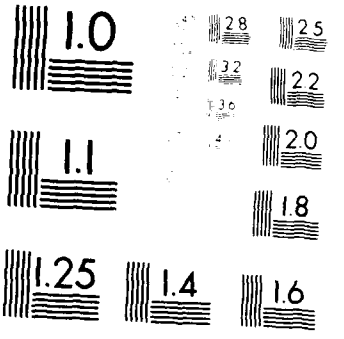

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FINAL REPORT

STUDIES OF THE FUNDAMENTALS OF SOLID-STATE BATTERIES

Contract No. N00014-86-C-0783

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ABSTRACT

Studies of Li/TiS_2 cells utilizing poly[bis(methoxyethoxyethoxide) phosphazene] (MEEP) based polymer electrolytes have demonstrated the excellent potential of this inorganic polymer electrolyte for use in solid-state rechargeable Li batteries for applications at or near room temperature. A major drawback of the MEEP electrolyte has been its lack of dimensional stability, manifested in its tendency to flow. This flow property prevented the preparation of thin film solid electrolytes. A solution to this problem has been found in this program by blending MEEP with poly(ethylene oxide), PEO, which resulted in novel mixed polymer electrolytes exhibiting superior mechanical stability and high conductivity. We have also developed a technique to fabricate solid-state cells with the pure MEEP electrolyte by supporting it on a thin, porous matrix comprising a fiberglass separator.

At room temperature, the 50 w/o MEEP + 50 w/o $PEO/LiClO_4$ exhibited about 400 times higher conductivity than $PEO/LiClO_4$. At 50 and 100°C, this mixed electrolyte showed a conductivity which is about 10 times higher than that of $PEO/LiClO_4$. The discovery of these mixed polymer electrolytes provides a new approach to the preparation of improved electrolytes for all-solid-state batteries.

The discharge of Li/TiS_2 cells utilizing "matrix supported" cells was better than that of any polymer electrolyte cells so far reported. Recharge efficiency of these cells at room temperature was poor, which suggests further fundamental studies on Li rechargeability in solid-state batteries.

The rate-capability of Li/TiS_2 cells utilizing the MEEP-$PEO/LiClO_4$ mixed electrolyte at 50 and 100°C was significantly better than that of cells containing $PEO/LiClO_4$. Thus, the former cells at 0.25 mA/cm^2, at 50°C, exhibited a utilization of 0.30 mAh/cm^2 while the cells containing $PEO/LiClO_4$ could not be discharged at this rate. The discharge performance achieved in a MEEP-$PEO/LiClO_4$ cell at 100°C has been better than any thus far reported in polymer electrolyte batteries.

Recommendations for a Phase II program include:

- Optimization studies to improve the dimensional stability of the MEEP electrolyte by mixing it with PEO or poly(propylene oxide) of different molecular weights, by supporting MEEP on a fiberglass or similar matrix, and by crosslinking MEEP with poly(ethylene glycol).

- Electrochemical and spectroscopic studies to characterize electrode reversibility, electrode/electrolyte interface, stability domain of the electrolyte and polarization behavior of the electrodes.

• Fabrication and characterization of both experimental and prototype cells containing Li, Li alloy or Li insertion anodes, dimensionally improved MEEP-electrolyte, and TiS_2 and other rechargeable cathodes.

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1.0 INTRODUCTION

There has been considerable recent interest in the design and development of all-solid-state, rechargeable Li batteries utilizing polymer electrolytes (1-3). The foundation for this rapidly growing field was laid by the discovery of significant Li^+ conductivity in the complexes of Li salts with organic polymers, such as PEO, by Armand et al. (4). Prominent examples of PEO-based polymer electrolytes are $(LiCF_3SO_3)_n \cdot PEO$, $(LiBF_4)_n \cdot PEO$ and $(LiClO_4)_n \cdot PEO$. In each of these complexes optimal conductivity is found when the value of n is ~0.125. They have exhibited conductivities of 10^{-7} to 10^{-4} $ohm^{-1}cm^{-1}$ in the temperature range of 40 to 100°C. Such conductivities are low in comparison to organic electrolytes which usually show values between 10^{-2} and 10^{-3} $ohm^{-1}cm^{-1}$. Nevertheless, the ability to fabricate thin films of the polymer complexes, which effectively shorten the distance for Li^+ migration during cell discharge, has stimulated consideration of these polymers as electrolytes for solid-state Li batteries. The availability of a number of highly reversible solid cathode materials such as TiS_2 and V_6O_{13}, which undergo Li insertion reactions, has served as additional impetus for the development of all-solid-state, rechargeable Li batteries.

All-solid-state Li batteries comprising polymer electrolytes have several potential advantages over their conventional liquid electrolyte counterparts. These include:

- Long shelf life, due to very little or no self-discharge.

- Long cycle life, due to the absence of significant anode passivation or dendrite formation.

- Easy fabrication of high voltage batteries in bipolar series connected arrangement, due to the absence of electrolyte leakage.

- Dimensional flexibility, enabling battery fabrication in many geometries.

- Ability to accommodate high temperature excursions; PEO-based batteries can operate satisfactorily at least up to 140°C.

- Component simplifcations, leading to mechanically stable, geometrically conforming devices.

A number of Li^+ ion-conducting polymer solid electrolytes are presently known (3). Among these the complexes of Li salts with PEO are the ones most frequently studied in connection with full cell development (1,2).

Because of low conductivity at room temperature, cells containing PEO-based electrolytes can be operated at reasonable current densities only at high ambient temperatures, around 100°C. The cells studied include $Li/(LiX)_n \cdot PEO/TiS_2$ and $Li/(LiX)_n \cdot PEO/V_6O_{13}$. The Li/TiS_2 cells were cycled more than 250 times at 0.5 to 1.0 mA/cm^2 at temperatures between 80 to 100°C (1). There have also been attempts, by the joint French-Canadian research group (1), to develop polymer electrolytes capable of operating at ambient temperatures. These electrolytes, whose compositions have not been disclosed, were employed in Li/MoO_2 and primary Li/MnO_2 cells achieving only very low current densities between 3 to 20 $\mu A/cm^2$.

The discovery of significantly high Li^+ conductivity in the complexes of poly[bis-(methoxyethoxyethoxide)phosphazene], or MEEP, I

$$[-N{=}P(OC_2H_4OC_2H_4OCH_3)_2]_n$$

I

with Li salts such as $LiCF_3SO_3$ represents a major development in the field of polymer electrolytes (5). The conductivity maximum for these complexes are obtained for compositions $MEEP \cdot (LiX)_{0.25}$, where LiX is a Li salt such as $LiCF_3SO_3$ and $LiBF_4$. Since these electrolytes exhibit 1 to 3 order of magnitude higher conductivity than those of the PEO complexes, it was expected that Li cells containing MEEP-electrolyte would have considerably better discharge rate capabilities at or near room temperature than those consisting of other polymer electrolytes. Consequently, this Phase I program was concerned with studies of a $Li/(LiX)_n \cdot MEEP/TiS_2$ cell, where $(LiX)_n$ is $LiClO_4$ or $LiCF_3SO_3$. The major focus of these studies was to demonstrate the feasibility of fabricating and testing full cells based on this inorganic polymer electrolyte, and to identify the various factors which affect their performance at or near room temperature.

The results of Phase I studies have been extremely promising. The usefulness of the MEEP-Li salt complex as electrolyte for solid-state Li batteries for applications at or near room temperature has been demonstrated. The poor dimensional stability of the MEEP-Li salt complex, which prevented the preparation of thin film solid electrolytes, has been mitigated by supporting this electrolyte on a porous fiber glass matrix. Li/TiS_2 cells constructed with this matrix-supported MEEP-electrolyte have shown outstanding discharge capabilities at room temperature. In addition, new polymer electrolytes exhbiting high conductivity have been prepared by blending Li salt complexes of PEO and MEEP. This discovery of mixed polymer electrolyte technology appears to provide a new direction in polymer electrolyte-containing all-solid-state battery technology.

2.0 ACCOMPLISHMENTS IN PHASE I

The primary objective of the Phase I program was to lay the foundation for a systematic investigation of solid-state batteries by characterizing the electrochemical behavior of cells of the type, $Li/(LiX)_n \cdot MEEP/TiS_2$.

We describe in the following sections the degree to which the Phase I objectives have been met, including the two major discoveries which have the potential to dramatically improve the performance of solid-state, rechargeable Li batteries operating at or near room temperature.

2.1 Experimental Section

The MEEP-electrolyte, containing MEEP and $LiCF_3SO_3$ with a weight ratio of 1 to 0.14 was obtained from Ethyl Corporation and hereafter referred to as MEEP, is a sticky material which gradually flows at room temperature. It was dried under vacuum for about 4 hours prior to use. PEO ($Mw = 5x10^6$) was obtained from Polysciences, Inc. $LiClO_4$ (Alfa-Ventron) was dried overnight under vacuum at 180°C and $LiCF_3SO_3$ (Ozark-Mohoning) was used as-received. Solutions were prepared by adding weighed quantities of polymer and the Li salt to acetonitrile under stirring. Care was taken to degas the solution at the end of stirring to prevent the formation of pinholes in the thin films due to trapped gas bubbles. Electrolyte films were cast by pouring known volumes of the polymer solution of desired concentrations onto Teflon dishes of known area and slowly evaporating the solvent at ambient temperature inside the glove box. Films with reproducible thickness can be prepared in this way. For example, to obtain films of $PEO/LiClO_4$ of 4 mil thickness, about 0.5 ml/cm^2 of 4 w/o solution was necessary. The films were dried overnight under vacuum at 100°C.

Conductivity data were obtained from analysis of complex impedance spectra between 5 Hz and 200 kHz. A lock-in frequency analyzer (PAR 5204) in conjunction with an oscillator (Gen-Rad 1310-B) was employed for this purpose (6). Conductivities at room temperature were also determined with a PAR 378 AC impedance system. The thin film electrolytes were held between two stainless steel ion-blocking electrodes of 1.8 cm^2 area. Resistance readings were taken after equilibrating the conductivity cell for one to two hours at the selected temperatures.

Infrared spectral analysis on the electrolyte films was carried out with an IBM system 9000 FTIR spectrometer. Scanning electron microscopic studies were performed with an AMR 1200 microscope. Care was taken during these studies to insure that the sample electrolyte films were not exposed to moisture.

Experimental Li/TiS_2 cells were fabricated with Li anodes, made by pressing 10 mil thick Li foils onto Ni screens. Cathodes were prepared by mixing TiS_2, synthesized in-house, with 20 w/o of $PEO/LiCF_3SO_3$ or $PEO/LiClO_4$ in acetonitrile. The $PEO:LiCF_3SO_3$ and $PEO:LiClO_4$ weight ratios were maintained at 2.3 and 3.3, respectively, so that the O/Li^+ ratio in each case was 8. To facilitate dispersion and prevent agglomeration of TiS_2, a small amount of Freon was added to the above mixture. The mixture was smeared onto 1 mil thick 1 cm x 2 cm Ni shims. Care was taken to distribute the TiS_2 uniformly over the entire cathode surface. However, since the amount of TiS_2 was very small, it was difficult to achieve a uniformly thick cathode layer in these early studies. Typical weights of TiS_2 were between 15 to 20 mg per 2 cm^2 of the electrode. The cathodes were dried by placing them under vacuum for about 3 hours. The Li anodes were made slightly larger than the cathodes, both in dimension and in capacity, so that the cells were all limited by the capacity of TiS_2 present on the cathode. Initially, cathodes were made by pasting the TiS_2-electrolyte mix on expanded Ni screens. But, it became clear that the cells were shorting due to the sharp edges of the screens, cutting through the electrolyte and making contact with the anode. Later, 1 mil thick Ni foil was employed as the cathode substrate after etching them shortly in HNO_3 to facilitate bonding between the cathode materials and the Ni shim. The cathode materials were applied only to one side of the foil.

The following procedures were employed to construct Li/TiS_2 cells with pure MEEP-electrolyte. Since the flowing nature of the MEEP-Li salt complex makes casting of thin films of defined geometry and thickness difficult, we devised two methods for laying the MEEP-complex between the anode and the cathode. i) A small amount of the complex, smeared over one side of the Li anode, was allowed to spread evenly inside the Ar filled glove box. This left a compact uniform film of the MEEP-complex on top of Li. Cells were made by just laying the cathode over the electrolyte-covered Li. The electrodes were held in place by putting a small weight on top of the electrode package. We call this type of cell the "unsupported MEEP cell". Since the electrolyte can flow, the electrode package was kept on its flat side and placed inside an air-tight glass cell holder containing tungsten leads for electrical connections and sealed via O-ring joints. ii) The "matrix supported" cells were prepared by spreading the electrolyte over one face of the Li anode and placing a 2 mil thick fiberglass mat (porosity 90%, Mead Paper Co.) over it. The TiS_2 cathode was placed on top of the fiberglass mat. The MEEP layer was left overnight to level off and wet the fiberglass separator.

All other cells utilizing PEO and PEO-MEEP mixed electrolytes were fabricated by sandwiching the electrolyte film between the anode and the cathode. Some of the cells were also made with Li reference electrodes to monitor the individual electrode potentials. The electrode packages of these and the "supported MEEP" cells were secured between steel plates, held tightly by compression springs, and placed in the cell holders. A sche-

matic of this cell design is depicted in Figure 1. Cells were thermostated inside an air oven and discharged and charged galvanostatically without any rest period between the half cycles. Data collection and retrieval were performed with the aid of Bascom-Turner (series 8000) recorder equipped with microprocessor accessories.

The preparation of PEO-MEEP mixed polymer electrolytes is described in detail in Section 2.2.3.

2.2 Results and Discussion

2.2.1 Performance of the Unsupported Li/MEEP/TiS_2 Cell

Discharge/charge performance of an "unsupported MEEP" cell at room temperature is depicted in Figure 2. The initial open-circuit potential of the cell was about 2.7V. The capacity delivered by this cell at a constant current of 0.10 mA (current density = 0.05 mA/cm^2) was 0.61 mAh or 16% of the theoretical cathode capacity. The specific utilization of the cathode 0.30 mAh/cm^2. The load voltage was as high as that expected for a Li/TiS_2 cell, with a mid-discharge voltage of 2.0V. This represents a significantly better performance than that of cells prepared with the PEO/$LiClO_4$ and PEO/$LiCF_3SO_3$ electrolytes (see later). Neither of the PEO electrolyte cells could be operated at room temperature. On the other hand, Li/MoO_2 cells with undisclosed polymer electrolytes, reported by the French-Canadian group, operated at 27°C and ~0.01 mA/cm^2, yielded utilization of ~10% for a cathode having the same theoretical capacity as ours (1).

The thickness of the in-situ prepared MEEP film in the "unsupported" cell was estimated to be ~5 mil. The cell showed poor rechargeability. It could be charged at half the discharge rate to only about 30% of the discharge capacity. This is evidently a poor charging efficiency. It appears that a much lower current is desirable for a full charging of the cell at room temperature. The cell package was subjected to a pressure of only 0.5 psig, since we had suspected that a higher pressure would force the MEEP to flow out of the cell package and cause shorting. The poor charging might have been due to insufficient stack pressure and/or poor interfacial transport.

These results clearly demonstrate the feasibility of ambient temperature solid-state Li battery with MEEP electrolyte for low rate applications. Improved electrolyte film incorporation techniques might yield better performance than what has been achieved so far.

The cycle performance of the above cell at 50°C is illustrated in Figure 3. At 1.0 mA (current density = 0.50 mA/cm^2) the cell delivered a capacity of 0.50 mAh. In sharp contrast to the behavior at room temperature, the coulombic balance between the charge and discharge was very close

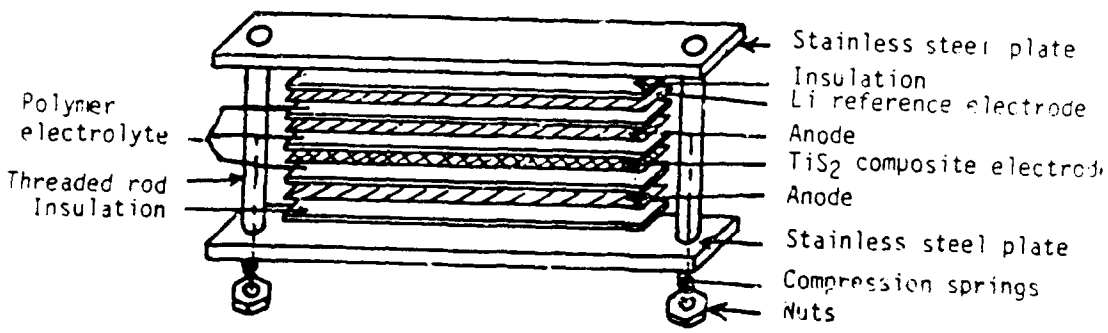

Fig. 1. Schematic representation of a Li/TiS_2 solid-state cell.

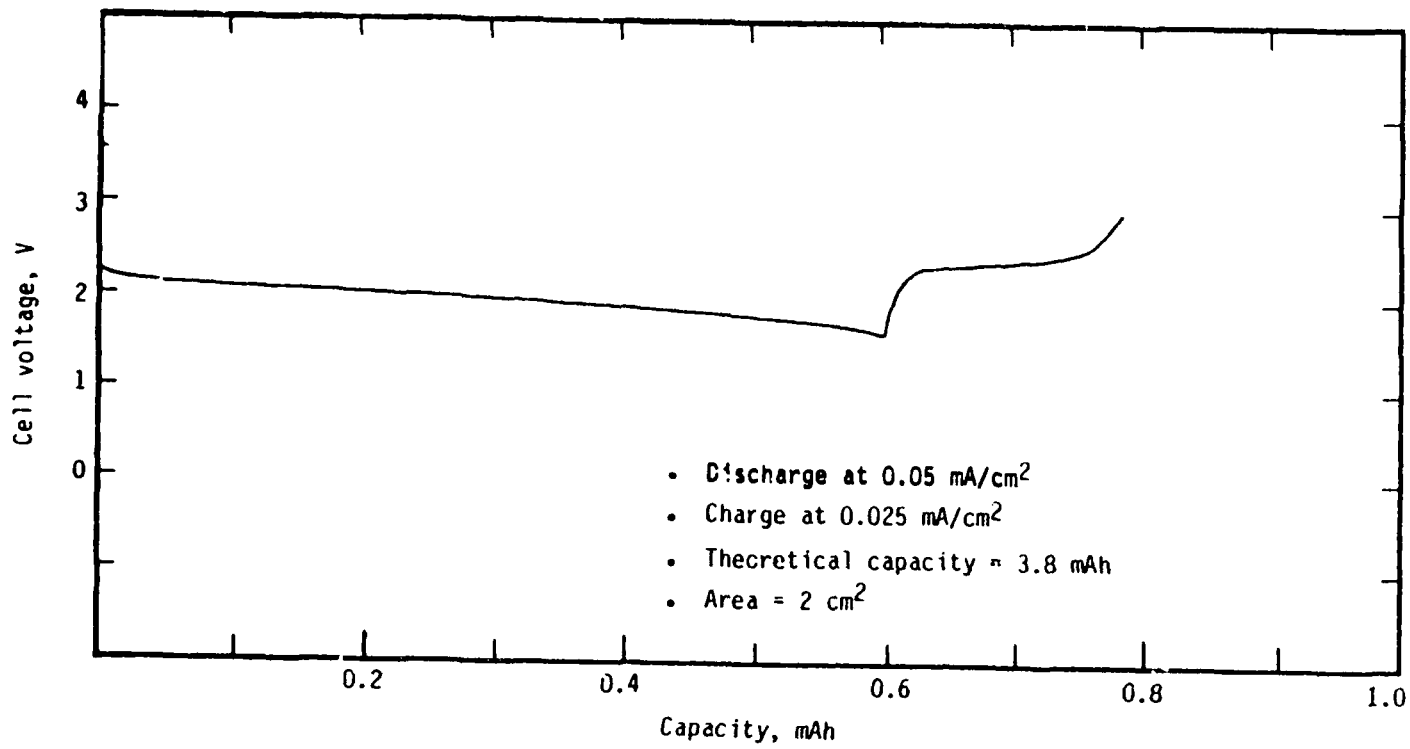

Fig. 2. Room temperature performance of a Li/MEEP/TiS_2 cell.

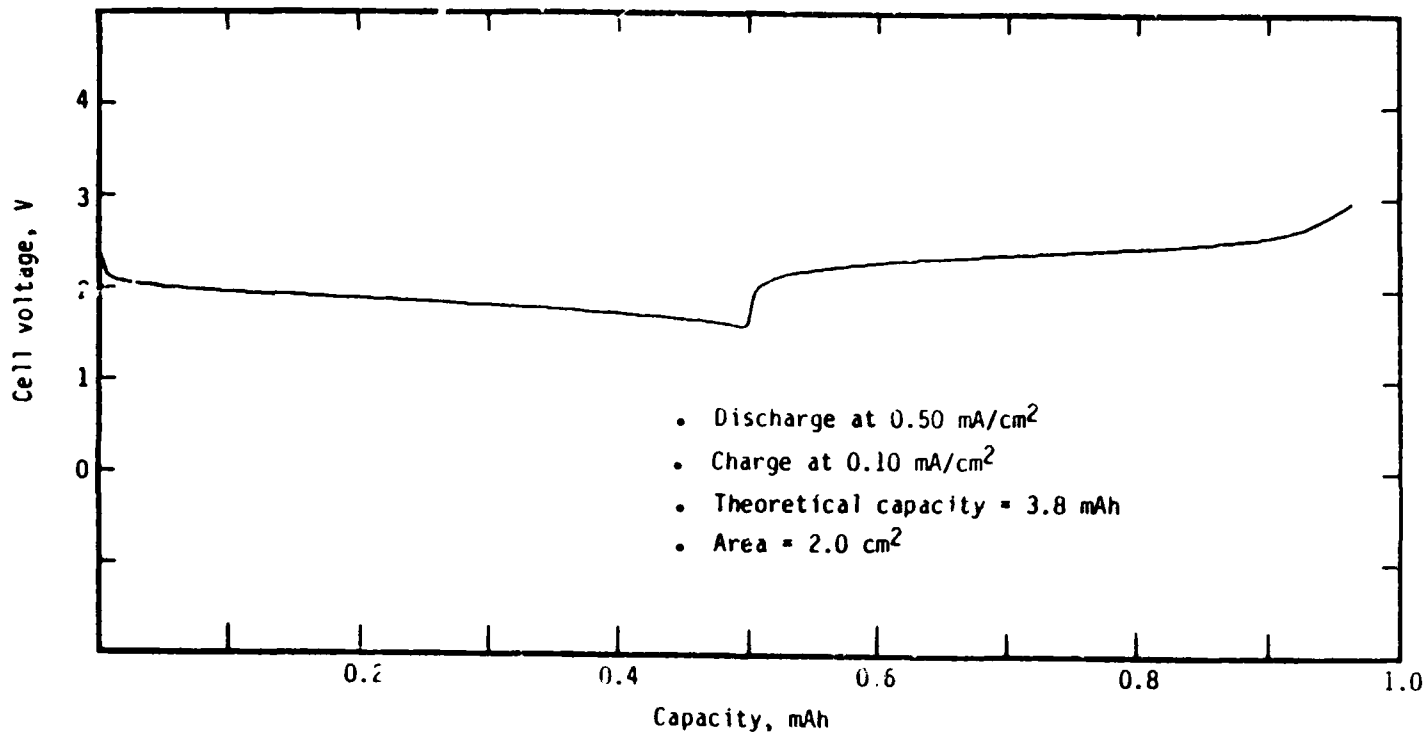

Fig. 3. Performance of Li/MEEP/TiS_2 cell at 50°C.

to 100%. The charging rate was 0.10 mA/cm^2. We shall see from later results that the performance of this cell at 50°C is far superior to that of the Li/PEO-$LiClO_4$/TiS_2 and the Li/PEO-$LiCF_3SO_3$/TiS_2 cells, which could not be discharged at this current. These PEO electrolyte cells delivered less than 1% of the available capacity, even at a discharge rate as low as 0.05 mA/cm^2.

The "unsupported MEEP" cell was also discharged and charged at 100°C. At a discharge current of 0.50 mA the cell delivered 1.95 mAh, which is 50% of the theoretical cathode capacity. The cell developed shorting on charge and could not be fully charged (Fig. 4). It appeared that the MEEP-electrolyte oozed out of the cell package facilitating shorting of the cell.

Current-Potential Behavior of the "Unsupported" Li/MEEP/TiS_2 Cell at Room Temperature: Galvanostatic polarization measurements on the Li anode were carried out with a Li/TiS_2 cell containing a Li reference electrode, which was placed next to the Li anode. The cell had the configuration, Li/MEEP/Li/MEEP/TiS_2. It was subjected to a series of anodic currents followed by cathodic currents, each for brief periods (maximum 50s) till the potential attained steady values. Figure 5 presents the summary of these measurements. The overpotential values were not corrected for iR drop due to electrolyte resistance.

The overpotentials of the Li anode in the cathodic and the anodic directions were of similar magnitudes. However, at or above 0.50 mA/cm^2 in the cathodic direction, the cathode exhibited excessive polarization, preventing meaningful potential measurements at higher currents in the cathodic direction. From extrapolation of the linear portion of the anodic polarization curve an estimated value of 3×10^{-1} mA/cm^2 was obtained for the exchange current density. The current-potential data indicate features which call for further detailed studies, especially the origin of the high cathode overvoltage at current densities >0.5 mA/cm^2.

Open-Circuit Potential of the Li/MEEP/TiS_2 Cell vs. Temperature: The open-circuit potential (OCV) of the Li/MEEP/TiS_2 cell was measured as a function of temperature. The open-circuit potential of a fresh cell at room temperature was about 2.7V. However, the cell after one cycle assumed a room temperature OCV about 2.4V. This cell was later used as the vehicle for measuring the OCV vs. temperature relationship. The results are illustrated in Figure 6. From the slope of the linearized curve a ΔS of 206 J/^{o}K·eq was obtained. Prior studies on Li/TiS_2 cells containing liquid electrolytes have shown that the OCV decreases with increasing temperature. The reason for the opposite behavior in the solid polymer electrolyte cells is not understood.

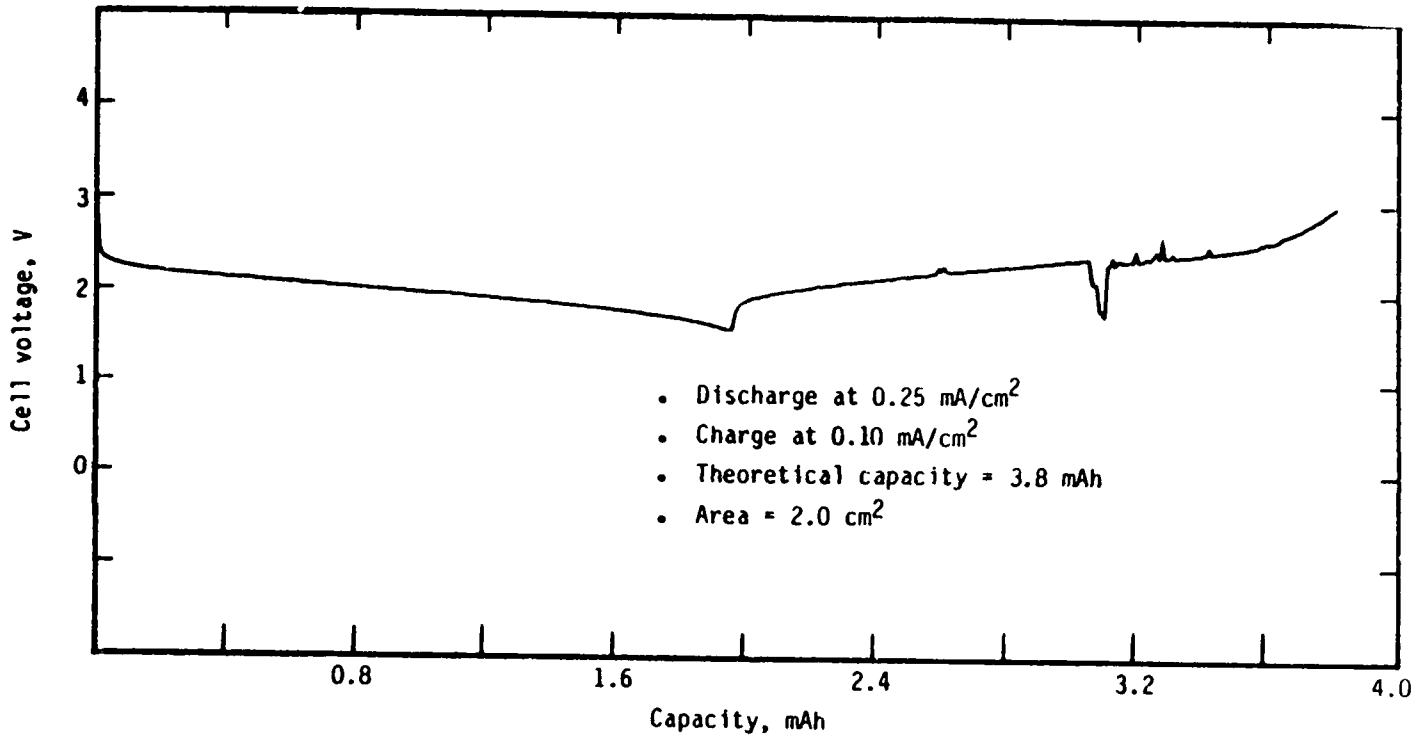

Fig. 4. Performance of a Li/MEEP/TiS_2 cell at 100°C.

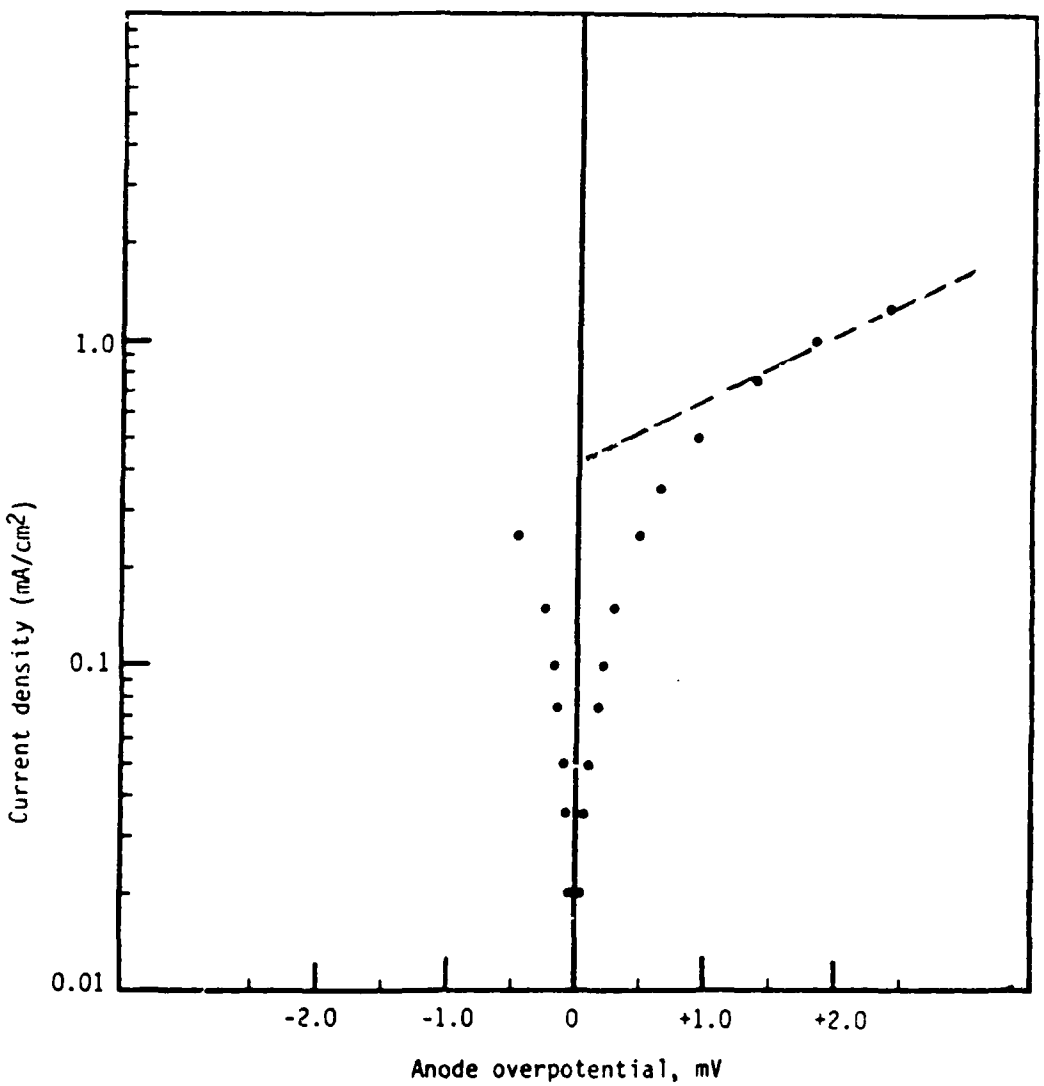

Fig. 5. Current-overpotential curves for the anode of the Li/MEEP/TiS_2 cell at room temperature.

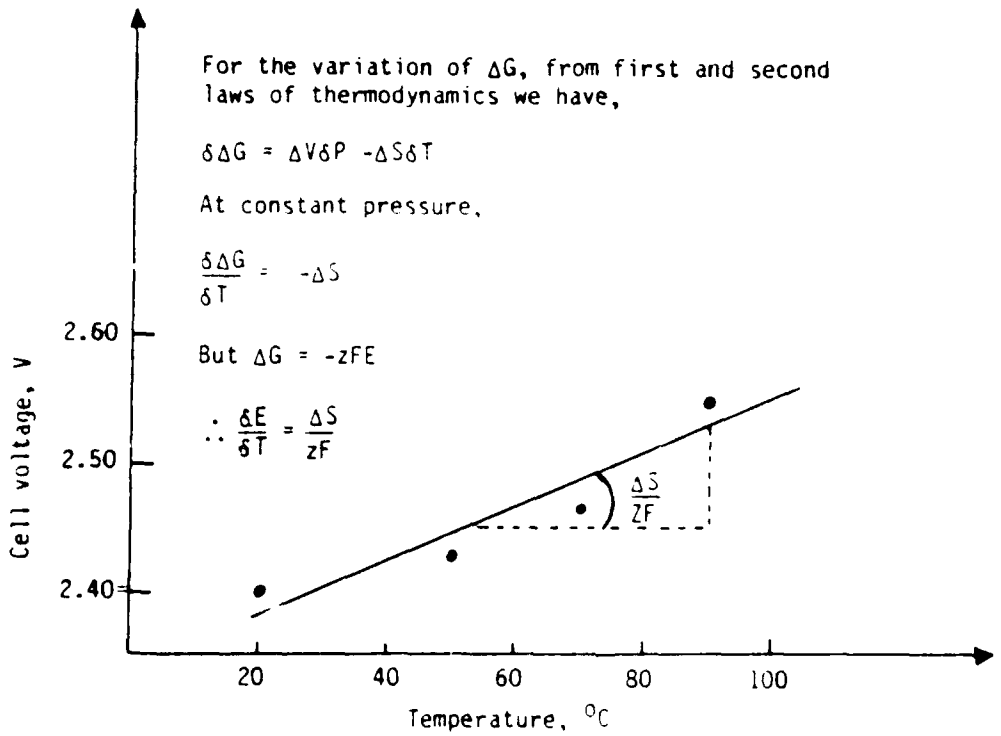

Fig. 6. Open-circuit potential of a Li/MEEP/TiS_2 cell as a function of temperature.

Problems of the MEEP-Electrolyte: Because of the difficulty in casting films of MEEP, the above studies with an electrode package in which MEEP was pasted on the Li anode were undertaken to assess the potential of MEEP as electrolyte for solid-state Li batteries. It was possible to operate the above cell by allowing it to lie on the flat side of the electrode package, so that the outflow of the electrolyte was minimized. This is not acceptable in practical cells. To be useful in a solid-state Li battery, the polymer electrolyte must possess physical integrity and dimensional stability as a thin film. These properties of the film must be maintained in a practical cell under various physical constraints such as varying temperatures, high electrode stack pressure, various cell orientations, reduced environmental pressure etc. It appears that the exceptional electrical properties of the MEEP electrolyte can be practically utilized only with improvements in its mechanical properties. Possible ways to improve the properties of the MEEP electrolyte include:

i) Supporting the MEEP electrolyte on a thin, highly porous but mechanically strong matrix such as fiberglass separator that would absorb and retain the electrolyte under pressure and at elevated temperatures.

ii) The use of reinforcements, materials which when added in a certain proportion to the MEEP would enhance its dimensional stability, without lowering the conductivity significantly. Traditionally, reinforcements are added to manufacture composite materials.

iii) Crosslinking of the polymer by adding a suitable reagent during polymerization, which will improve the mechanical properties of the polymers.

The first two improvements have been achieved in the Phase I program. The time constraints of Phase I did not permit any work related to crosslinking of MEEP. This will be performed in the Phase II program.

2.2.2 Use of Fiberglass Separator as Matrix Support for MEEP Electrolyte

We assembled a Li/TiS_2 cell using fiberglass paper as support for the MEEP electrolyte. As discussed in the Experimental Section, the electrolyte was incorporated by spreading it over one face of the Li and placing a 2 mil thick porous fiberglass paper. The cell was fabricated by placing the cathode over the separator and securing the cell stack between steel plates.

Figure 7 shows the room temperature discharge performance of this cell at 0.20 mA (0.10 mA/cm^2). The capacity obtained was 0.48 mAh, or 20% of the theoretical cathode capacity. This appears to represent the best room temperature discharge performance achieved so far with rechargeable, Li solid-state batteries containing polymer electrolytes. As mentioned

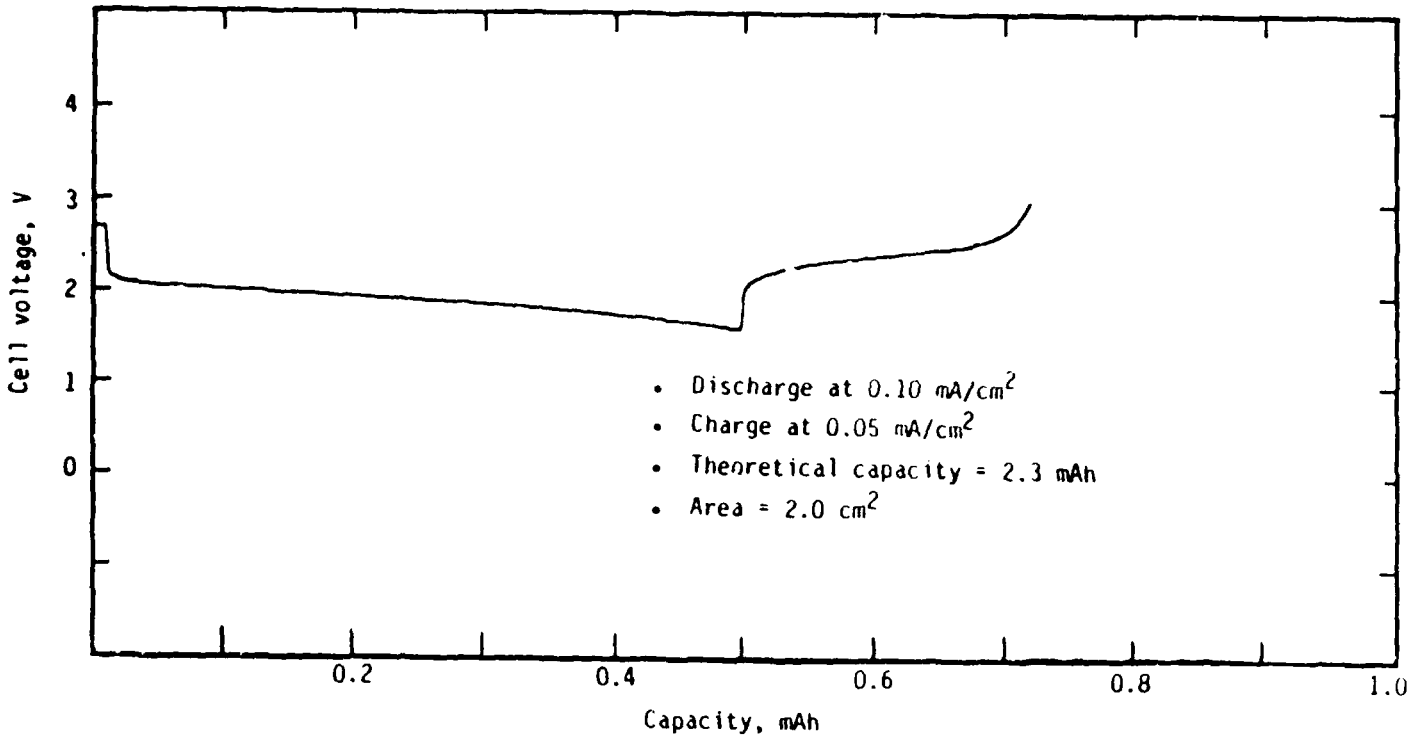

Fig. 7. Performance of a "supported" Li/MEEP/TiS_2 cell at room temperature.

The activation energy for conduction in MEEP/PEO-$(LiBF_4)_n$ was determined as a function of the ratio of the two polymers and the salt concentration (8). For the 55/45 polymer weight ratio, the activation energy below 60°C was insensitive to salt concentrations corresponding to n between 0.016 and 0.18. However, activation energy increased substantially when the amount of MEEP decreased from 70 w/o to 50 w/o. This behavior is consistent with higher plasticity for electrolytes having higher MEEP contents. Above 60°C, correlations between activation energy and electrolyte composition were not straightforward.

The complex impedance spectra of electrolytes using stainless steel blocking electrodes appear to reflect the degree of plasticity of the electrolytes. Conductivities of the electrolytes were calculated from such spectra. Figure 6a and 6b display the data for 55 MEEP/45 PEO-$(LiBF_4)_{0.13}$ at different temperatures. The AC frequency range was between 6 Hz and 100 kHz. For fresh electrolytes at room temperature, the Cole-Cole spectrum represented a semicircle with a spur at low frequencies. This represents an equivalent circuit in which the electrode capacitance is in series with a parallel combination of electrolyte resistance and its capacitance. With increasing temperature the semicircle gave way to the spur and at a temperature above the melting point of PEO only a straight line usually remained. At these temperatures, the capacitative component of the electrolyte appears to be negligible up to a frequency of 100 kHz. The high plasticity induced at temperatures above the melting point of PEO appears to decrease the dielectric relaxation times of the electrolyte so that in our frequency range of impedance measurement the electrolyte capacitance becomes negligible. In fact, as shown in Figure 6a, the electrolyte heated once to 80°C and then cooled to 20°C shows an impedance spectrum indicative

electron micrographs (SEM) show (Figs. 8 and 9) that the film surface is uniform, lacking significant, well-organized macrostructures of the types found in the films of PEO/$LiCF_3SO_3$ (see below). Small dots which are indicative of bubbles from poor degassing were noticed in the SEM pictures. We have also investigated a lower MEEP ratio such as 20 w/o; but, these composition showed lower conductivities. At a higher MEEP ratio such as 80 w/o, the films did not grow uniformly and a separation of the MEEP and the PEO phases was observed. It should be noted that we consider these studies carried out so far as preliminary and significant work regarding optimization of the mixed electrolyte compositions remains to be carried out.

MEEP was also added in various proportions to the PEO/$LiCF_3SO_3$ solution in acetonitrile. The films appeared similar to those of the PEO/$LiCF_3SO_3$ electrolyte and were fluffy and highly porous. SEM pictures revealed (Figs. 10 and 11) features typical of crystalline and highly structured phases as in PEO/$LiCF_3SO_3$. This sharp difference in the morphologies of the PEO/$LiClO_4$ and PEO/$LiCF_3SO_3$ films might explain the inferior performance of the cells containing the latter electrolytes (see later). Again, above 50 w/o of the MEEP, we could not obtain films of uniform texture. Separation of the MEEP and the PEO-electrolyte phases apparently occurred. Further studies are needed to determine the optimal composition ranges of the mixed polymer electrolytes containing $LiCF_3SO_3$.

The conductivities of the mixed polymer electrolytes showed some very interesting trends. Figure 12 compares the conductivities of PEO/$LiClO_4$, PEO/$LiCF_3SO_3$, MEEP/$LiCF_3SO_3$, 50 w/o MEEP + 50 w/o PEO/$LiClO_4$ and 50 w/o MEEP + 50 w/o PEO/$LiCF_3SO_3$, all determined by AC impedance techniques (6). It is apparent from the figure that, at all temperatures, the mixed polymer electrolytes have much higher conductivity than the pure PEO electrolytes. Although these values are lower than those reported for pure MEEP electrolyte, at temperatures above 50°C the conductivity of the mixed electrolyte system, especially that containing $LiClO_4$, is very similar to that of the MEEP electrolyte. The mixed polymer electrolyte containing $LiClO_4$ has higher conductivity than that containing $LiCF_3SO_3$. At room temperature, the conductivities of the MEEP/PEO/$LiClO_4$ electrolyte is about 400 times higher than that of the PEO electrolytes. For example, the conductivity of PEO/$LiClO_4$ at room temperature was 2.5×10^{-9} $ohm^{-1}cm^{-1}$, whereas that of the MEEP-PEO/$LiClO_4$ was 1.1×10^{-6} $ohm^{-1}cm^{-1}$. At 50°C the mixed electrolyte, containing $LiClO_4$, was about 10 times more conducting than PEO/$LiClO_4$. A ten times difference in conductivity was also found at 100°C between the mixed electrolyte and PEO/$LiCF_3SO_3$. Although the $LiCF_3SO_3$-containing mixed-polymer complex has a lower conductivity than its $LiClO_4$ analog, conductivity of the former at all temperatures examined was higher than that of both PEO/$LiClO_4$ and PEO/$LiCF_3SO_3$ systems.

Discontinuities in the conductiviy-temperature curves such as those observed in the case of pure PEO/Li salt electrolytes (Fig. 12), are indicative of phase changes. Robitaille and Fauteux (7) have studied such

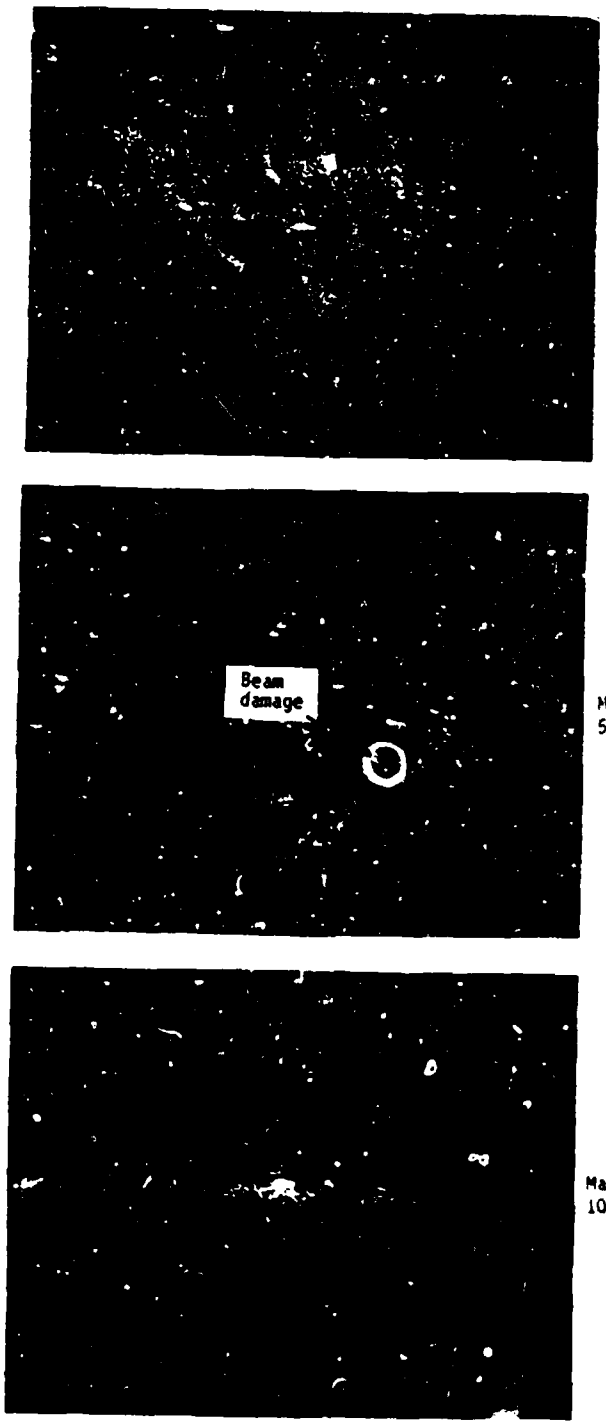

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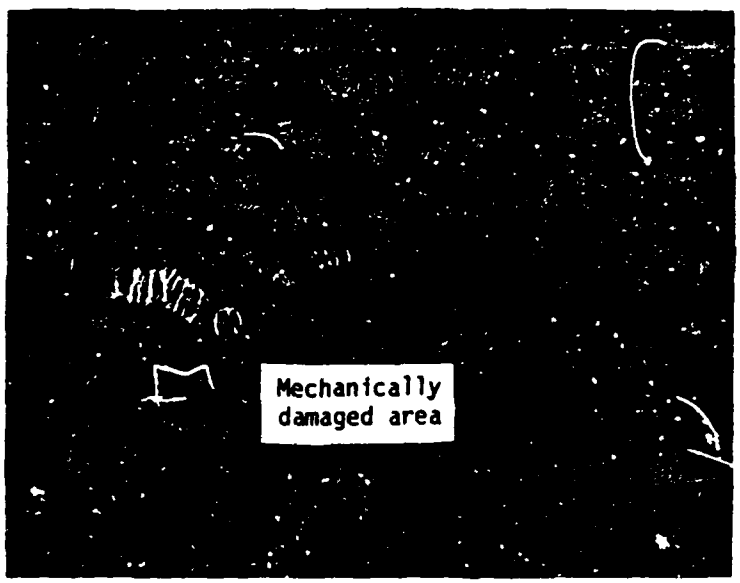
Fig. 8. SEM micrographs of 50 w/o MEEP + 50 w/o PEO-$LiClO_4$ electrolyte films.



Magnification
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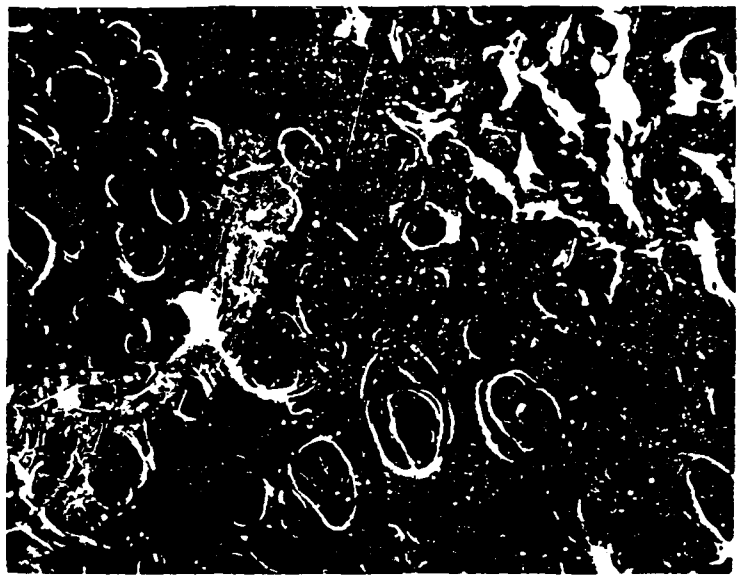
Fig. 9. SEM micrographs of PEO/$LiClO_4$ films.

Fig. 10. SEM micrographs of PEO/$LiCF_3SO_3$ films.



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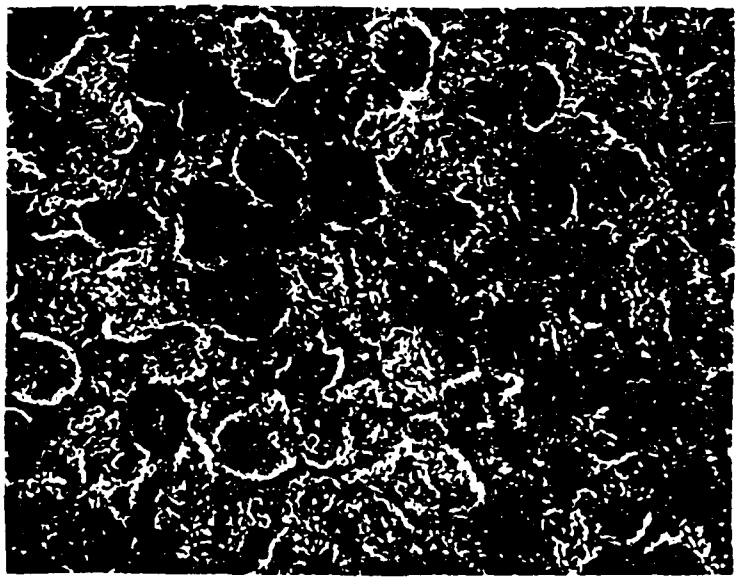

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Fig. 11. SEM micrographs of 50 w/o MEEP + 50 w/o PEO/$LiCF_3SO_3$ films.

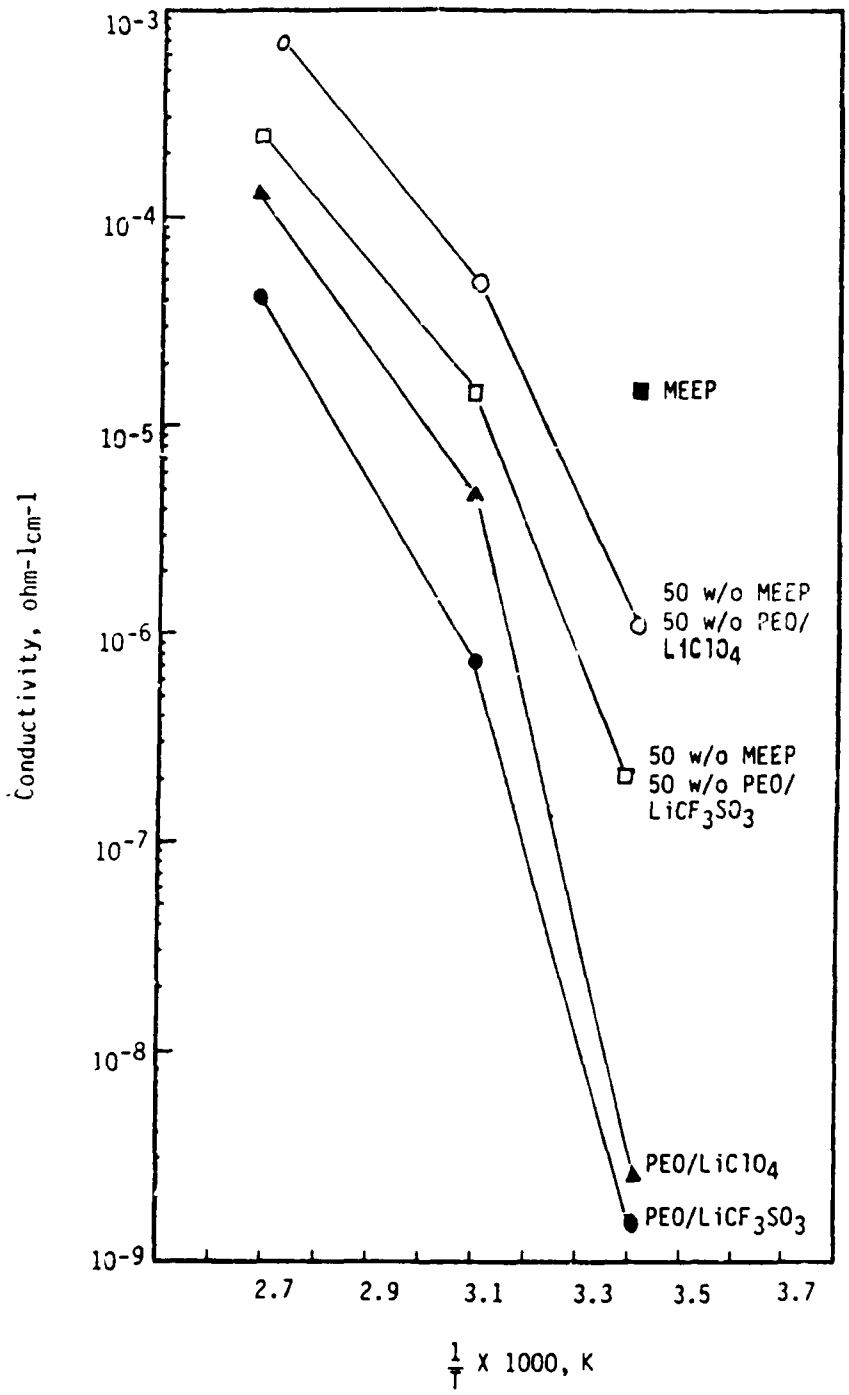

Fig. 12. Conductivities of various polymer electrolytes at different temperatures.

The open-circuit potentials of freshly prepared cells were between 2.8 and 2.9V, which on heating to 50°C declined slightly to values between 2.6 and 2.8V. Figure 15 shows typical constant current charge-discharge curves of a Li/TiS_2 cell using MEEP-$(LiClO_4)_{0.25}$ electrolyte supported in a fiber-glass separator paper. The cells were discharged to a voltage limit of 1.6V and charged to 3.0V. The data encompass three different rates at 50°C. The current densities were 0.05, 0.1 and 0.2 mA/cm^2 at the C/28, C/15 and C/7 rates. The cell delivered the capacities of 1.10, 0.45 and 0.28 mAh/cm^2, respectively, at these rates. Increasing the discharge temperature from 50 to 75°C more than doubled the capacity of the cell. The mid-discharge voltage was 2.1V, while the average charging potential was 2.5V. The coulombic efficiency during the cycling was between 90 and 100%.

Figure 16 shows the long-term cycling performance of a second Li/TiS_2 cell using MEEP-$(LiClO_4)_{0.25}$ supported on a fiber-glass paper matrix. The cell was cycled more than 200 times. The continuous decrease in capacity with cycling is somewhat typical of unoptimized laboratory cells in which the capacity loss is associated with several factors including cathode structural problems, inefficiencies in the recharging of the anode and cathode, and any number of mechanical reasons. However, the present data clearly show that the MEEP-based electrolytes are chemically and electrochemically stable in contact with Li and can be fabricated into long cycle life secondary Li batteries.

A knowledge of the overcharge and overdischarge behavior of a secondary Li cell, that is, discharge and charge into potential regions beyond where the normal electric current producing redox chemistry of the cell occurs, is important since such a condition could be encountered in the normal operation of a battery. Undesirable electrochemical reactions during overdischarge and overcharge can be detrimental to the stability of the cell. Figure 17 depicts that the cell can function normally even after a considerable extent of overcharge.

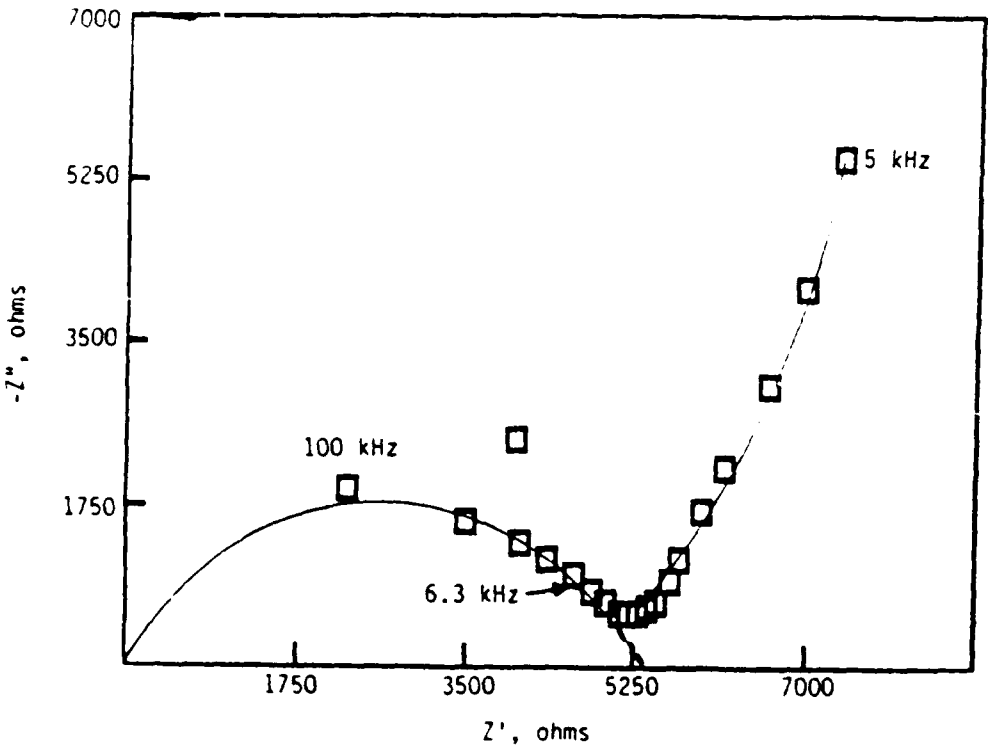

Fig. 13. Complex impedance plot of 50 w/o MEEP + 50 w/o PEO/ $LiClO_4$ mixed electrolyte at room temperature.

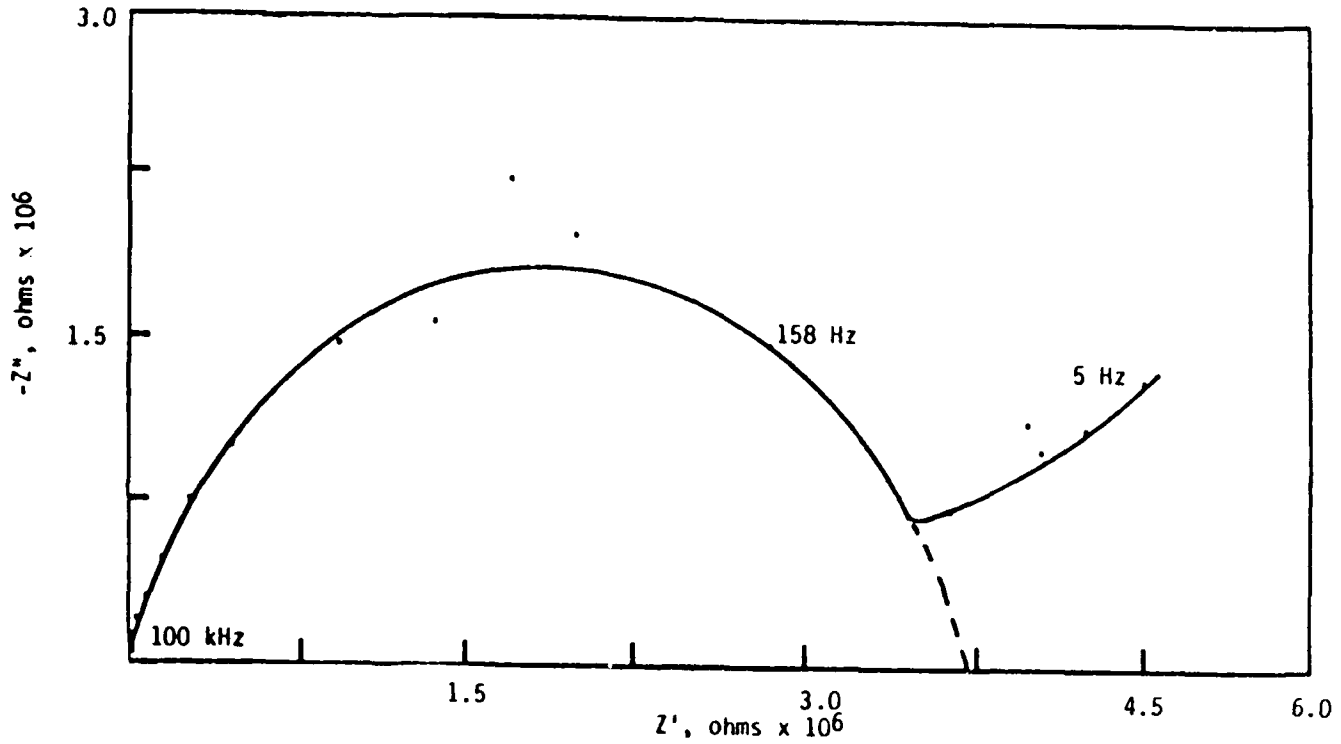

Fig. 14. Complex impedance plot of PEO/$LiCF_3SO_3$ electrolyte at room temperature.

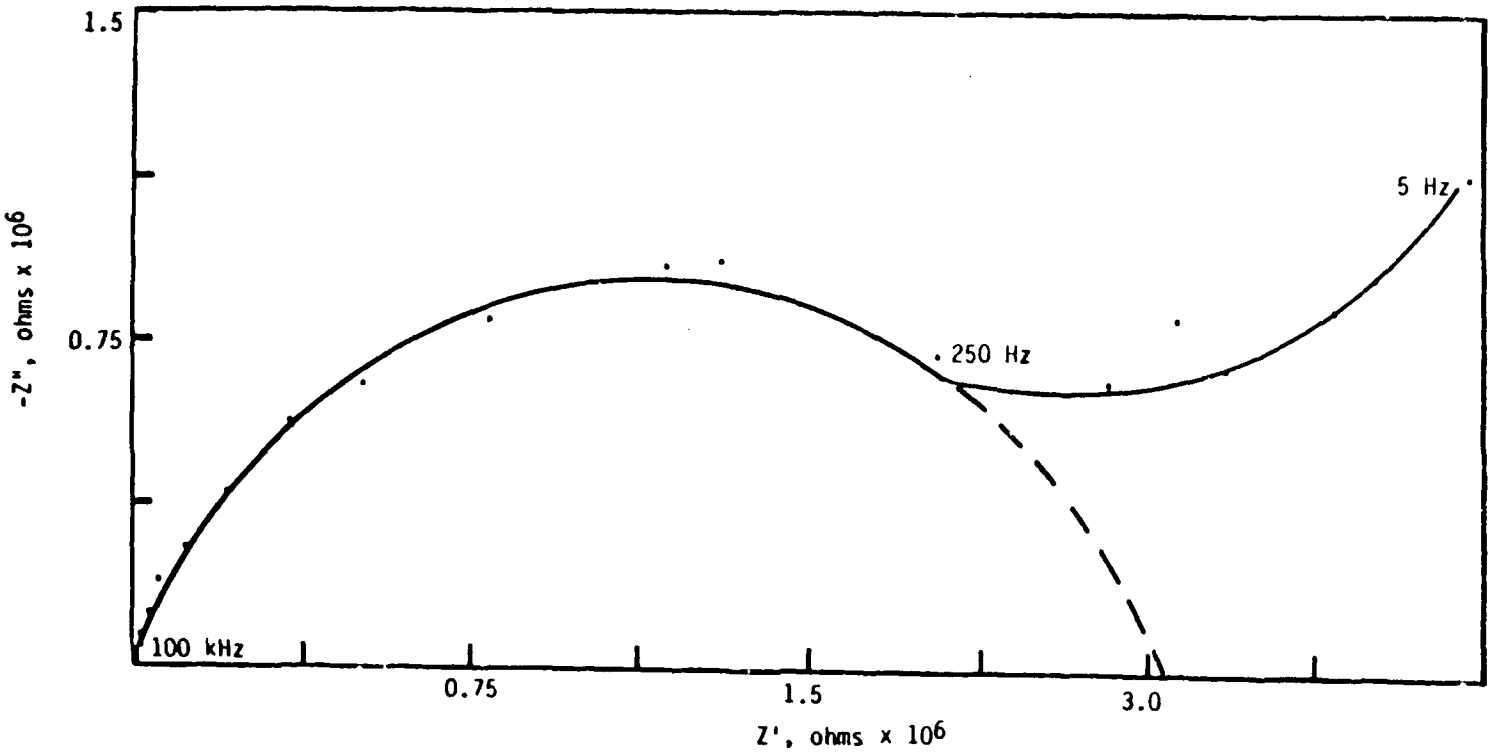

Fig. 15. Complex impedance plot of PEO/$LiClO_4$ electrolyte at room temperature.

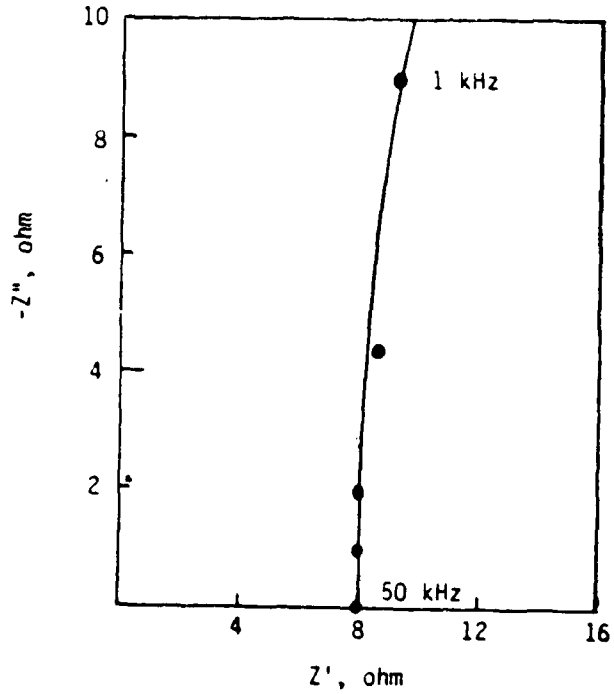

Fig. 16. Complex impedance spectrum of 50 w/o MEEP:50 w/o PEO/ $LiClO_4$ at 95°C.

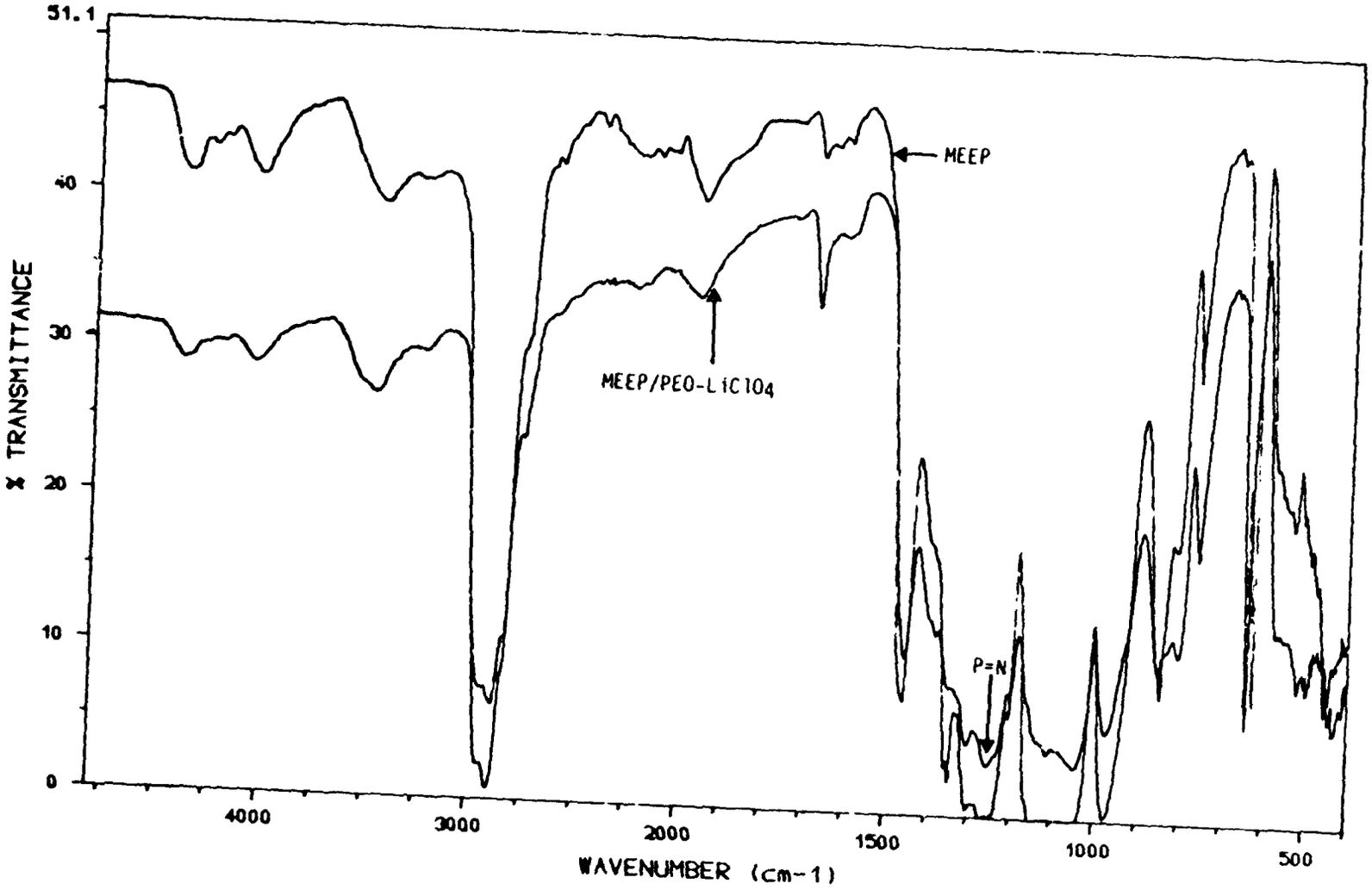

Fig. 17. Comparison of the FTIR spectra of MEEP-electrolyte and the MEEP/PEO-$LiClO_4$ electrolyte.

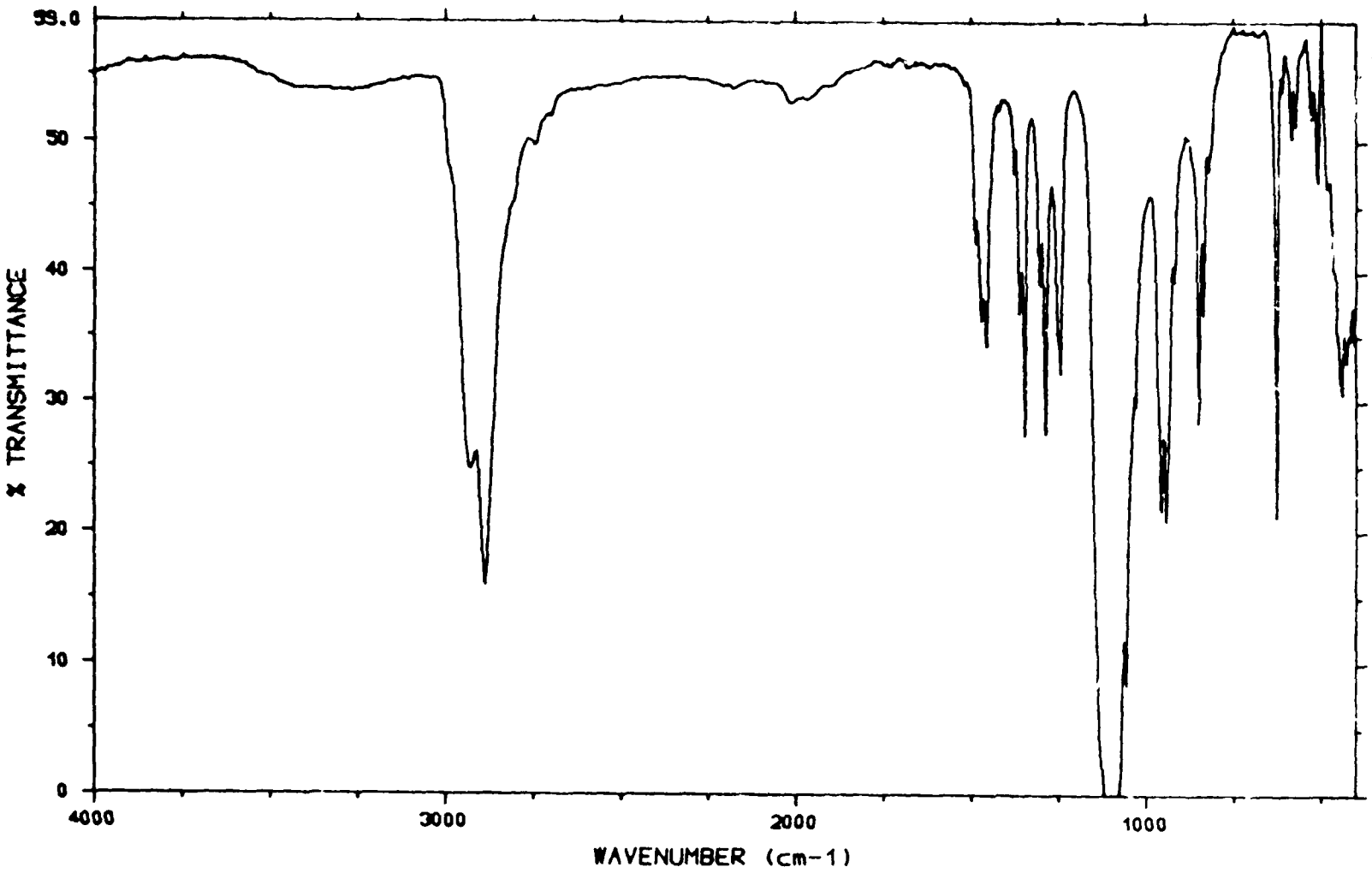

Fig. 18. IR spectrum of PEO/$LiClO_4$ electrolyte film.

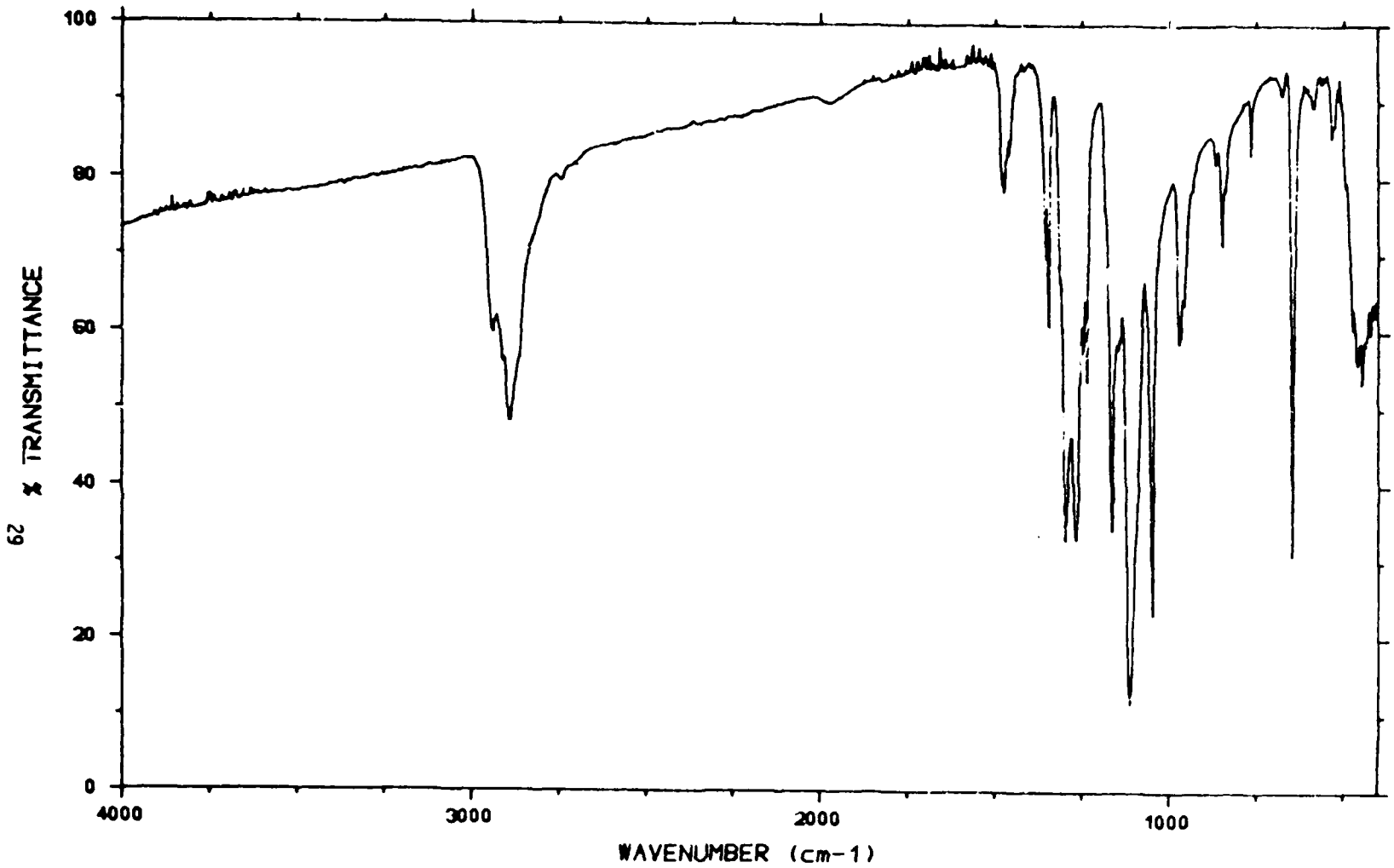

Fig. 19. IR spectrum of PEO/$LiCF_3SO_3$ electrolyte film.

The discharge/charge characteristics of the MEEP-PEO/$LiClO_4$ cell at 50°C is illustrated in Figure 20. The cell delivered a capacity of 0.62 mAh at 0.50 mA, which corresponds to a discharge current density of 0.25 mA/cm^2. The utilization of 0.30 mAh/cm^2 is significantly better than the performance of Li/PEO-$LiClO_4$/TiS_2 and the Li/PEO-$LiCF_3SO_3$/TiS_2 cells, and is similar to that of the "matrix-supported" Li/MEEP/TiS_2 cell at 50°C.

The capacity-rate behavior of a MEEP-PEO/$LiClO_4$ electrolyte cell at 100°C is depicted in Figure 21. The utilizations are excellent as compared to data presently available for polymer electrolyte batteries (5). At 1.0 mA constant current (0.50 mA/cm^2) the cell delivered 80% of the theoretically available cathode capacity, whereas at 4.0 mA (2.0 mA/cm^2) the cell delivered over 50% of the capacity. The latter translates to a specific utilization of 0.90 mAh/cm^2, which is one of the best discharge rate performance thus far obtained with polymer electrolyte batteries. Clearly, these data are preliminary and significant further improvement should be possible with additional optimization of the electrolyte composition and cell construction techniques.

Li/MEEP-PEO-$LiCF_3SO_3$/TiS_2 Cell at 100°C: We constructed a cell with a 50 w/o MEEP + 50 w/o w/o PEO/$LiCF_3SO_3$ electrolyte and the cycling performance of this cell at 100°C and 0.50 mA/cm^2 is illustrated in Figure 22. The cell delivered a capacity of 1.30 mAh, which is less than half of that delivered by the cell containing MEEP/PEO/$LiClO_4$ electrolyte. Inferior results were obtained with a Li/TiS_2 cell containing a 20 w/o MEEP + 80 w/o PEO/$LiCF_3SO_3$ electrolyte. At a discharge current density of 0.25 mA/cm^2 the cell delivered 1.16 mAh, or about 30% of the theoretically available cathode capacity (Fig. 23). Comparison of these results clearly shows the beneficial effect of higher MEEP content in the electrolyte.

Thus, our preliminary results indicate that the salt plays a significant role on the performance of these cells. Electrolytes containing $LiClO_4$ perform better than those containing $LiCF_3SO_3$. The correlations between the nature of the salt and electrolyte properties will be investigated in detail in Phase II.

2.2.4 Studies of Cells Containing PEO Electrolytes

The improved discharge rate capability of cells containing the mixed polymer electrolytes becomes apparent when we compare their performance with those of cells containing PEO/$LiCF_3SO_3$ and PEO/$LiClO_4$ electrolytes. Thus, cells containing these conventional polymer electrolyte have been evaluated to allow direct comparisons with the mixed electrolyte cells in the same laboratory test cells.

Li/PEO-$LiClO_4$/TiS_2 Cells: Experimental cells similar to those containing MEEP-PEO/$LiClO_4$ were constructed with PEO/$LiClO_4$ electrolyte. The TiS_2 cathodes contained 20 w/o PEO/$LiClO_4$ and 80 w/o TiS_2.

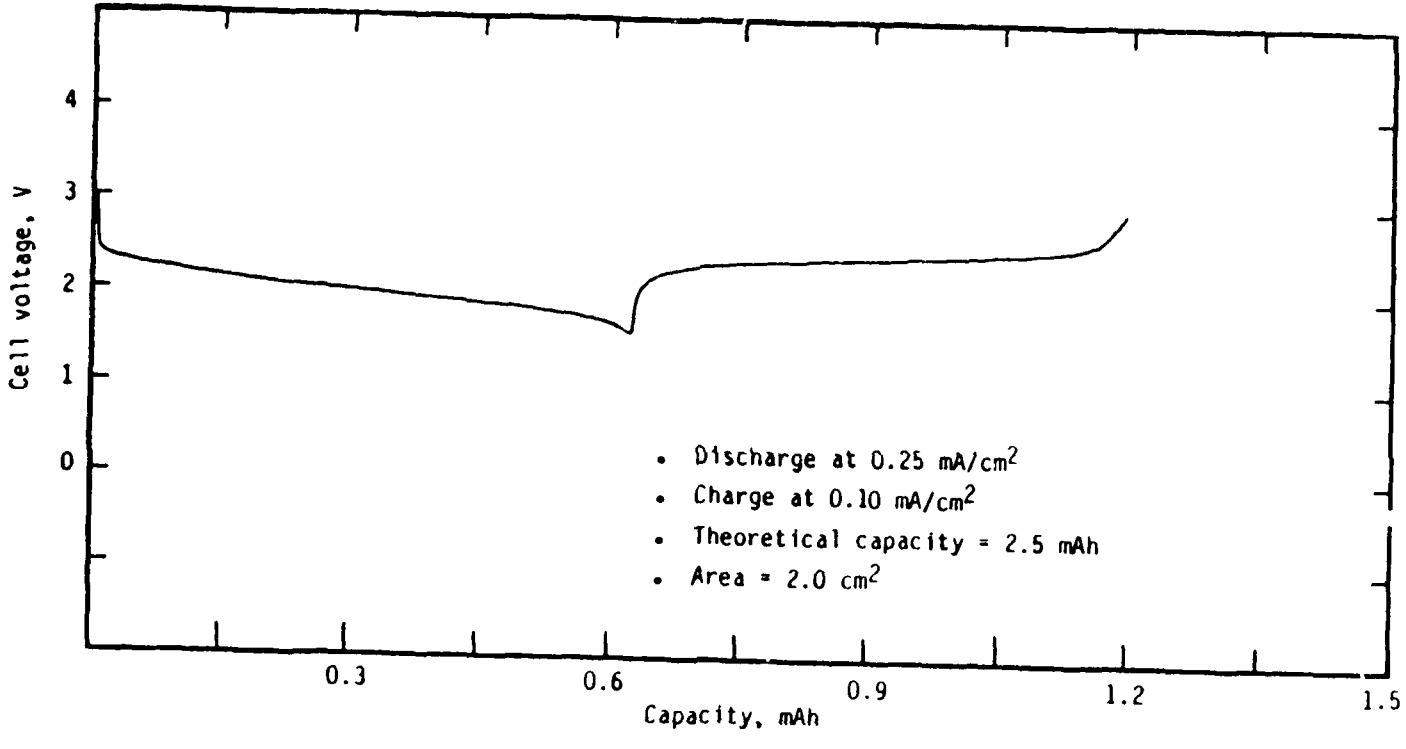

Fig. 20. Performance of a Li/MEEP-PEO-$LiClO_4$/TiS_2 cell at 50°C.

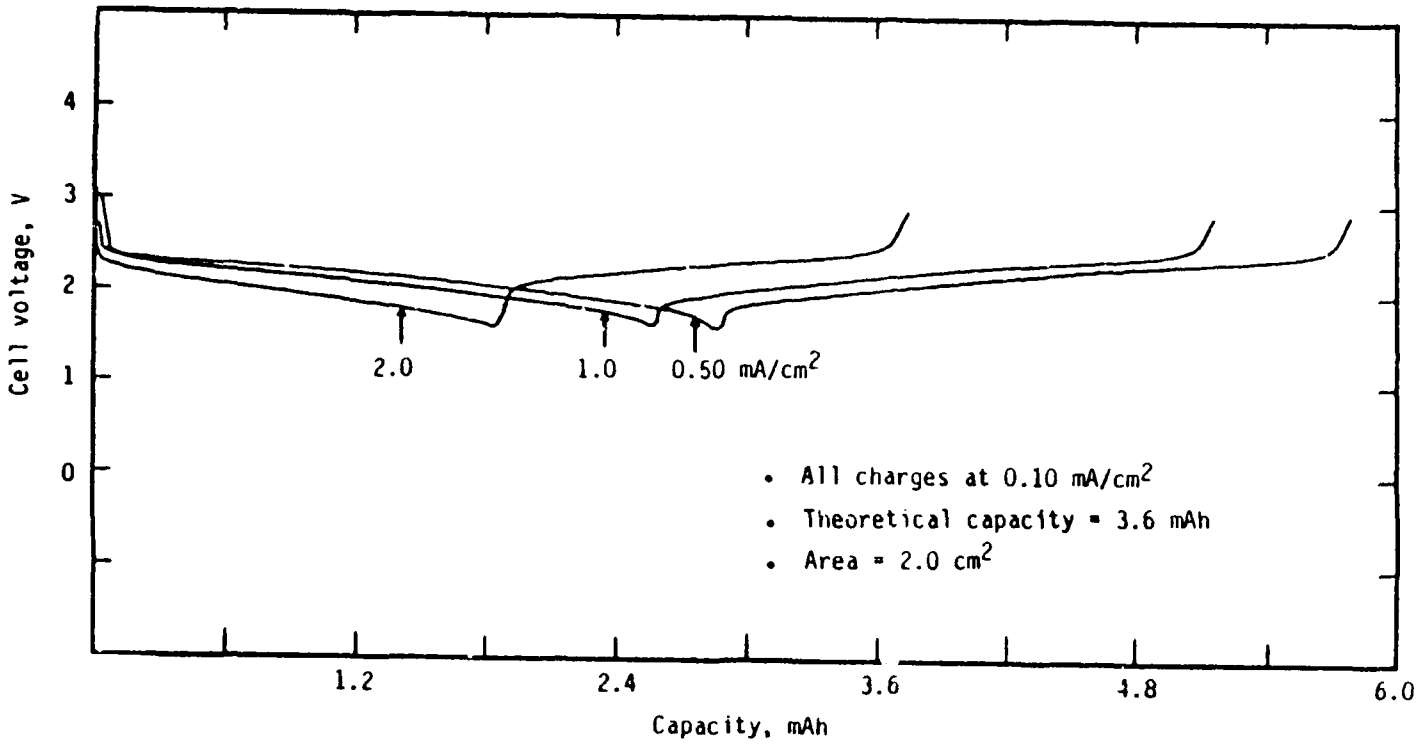

Fig. 21. Performance of a Li/MEEP-PEO-$LiClO_4$/TiS_2 cell at 100°C at different currents.

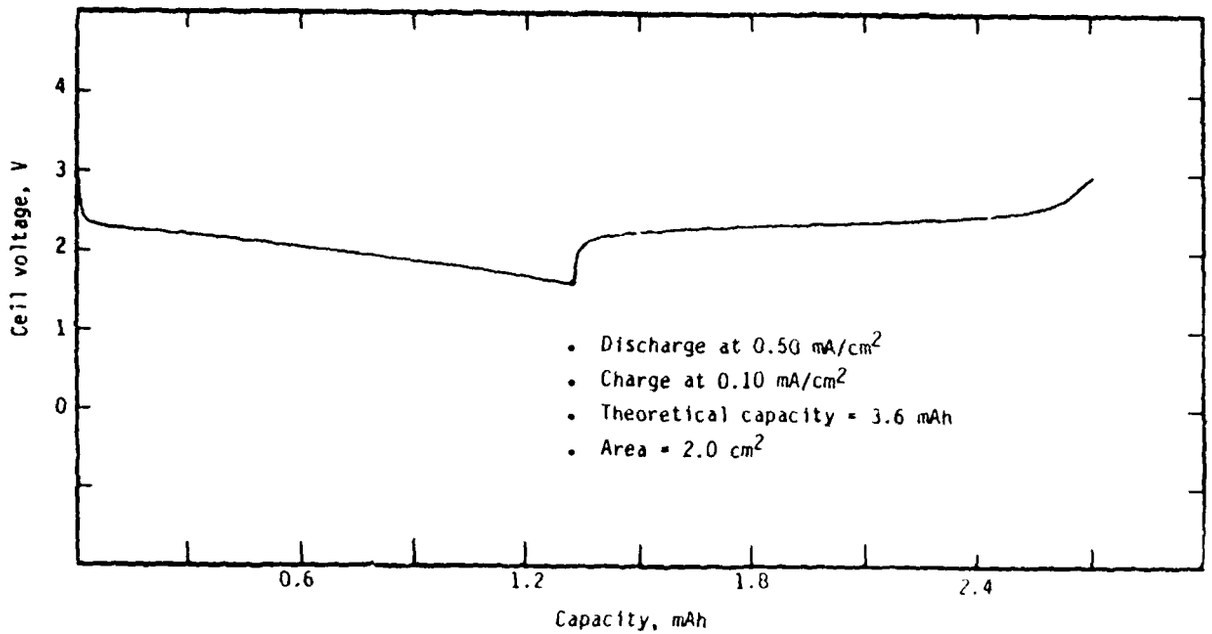

Fig. 22. Performance of a Li/MEEP-PEO-$LiCF_3SO_3$/TiS_2 cell at 100°C.

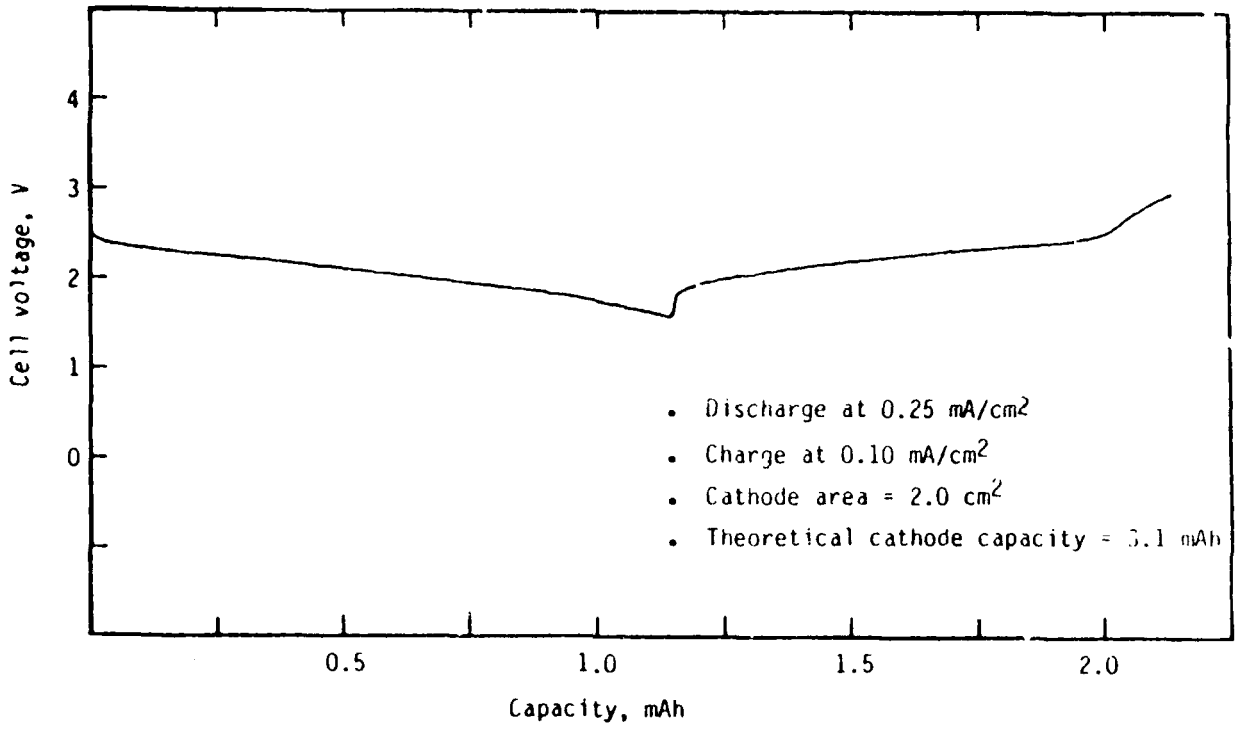

Fig. 23. Cycling performance of a Li/TiS_2 cell containing 20 w/o MEEP + 80 w/o $PEO/LiCF_3SO_3$ electrolyte.

Cells could not be discharged at room temperature even at the low current of 0.05 mA.

The discharge/charge performance of a cell at 50°C and 0.10 mA (0.05 mA/cm^2) is illustrated in Figure 24. The capacity delivered was less than 1% of the theoretical cathode capacity of 3.10 mAh. Clearly, the discharge capability of cells containing $PEO/LiClO_4$ is significantly inferior to that of cells containing MEEP and MEEP-PEO mixed electrolytes.

The capacity-rate behavior of Li/TiS_2 cells containing $PEO/LiClO_4$-electrolyte at two different current densities at 100°C is depicted in Figure 25. The utilization of the cathode at 1.0 mA/cm^2 discharge current density was 1.90 mAh, or approximately 60% of that of the Li/MEEP-PEO-$LiClO_4/TiS_2$ cell. This clearly demonstrates the advantage of the mixed polymer electrolyte.

Performance of $Li/PEO\text{-}LiCF_3SO_3/TiS_2$ Cells: These cells could neither be discharged at room temperature nor at 50°C even at 0.05 mA/cm^2.

The performance of a cell at three different current densities at 100°C is shown in Figure 26. The discharge capacity of this cell was significantly inferior to that of cells containing $PEO/LiClO_4$ or the mixed PEO-MEEP polymer electrolytes. This cell was constructed with a 4 mil thick electrolyte film, similar to the ones used in the cells discussed earlier. Even at such a low current density as 0.05 mA/cm^2, the cell delivered a capacity of only 0.40 mAh or 20% of the available capacity.

Polarization Studies of $Li/PEO\text{-}LiCF_3SO_3/TiS_2$ Cells: Galvanostatic polarization studies, similar to those described in Section 2.2.2, were also carried out with a $Li/PEO\text{-}LiCF_3SO_3/TiS_2$ cell, in this case at 100°C. The cell also contained a Li reference electrode to monitor the response of the individual electrodes. The summary of these measurements is contained in Figure 27.

From extrapolation of the linear portion of the polarization curves the exchange current densities for the anodic and cathodic processes at the Li anode were determined. The overpotentials were of similar magnitudes in both the anodic and the cathodic directions. Values between 0.3 and 0.4 mA/cm^2 were obtained for the exchange current densities. It is interesting to note that these values are similar to those of the $Li/MEEP/TiS_2$ cell (see Section 2.2.2) at room temperature, demonstrating the usefulness of the MEEP-electrolyte for applications at ambient temperature.

2.2.5 Extended Cycling of Polymer Electrolyte Cells

The primary objective in Phase I was to study the feasibility of Li solid-state cells containing MEEP-Li salt as the electrolyte and to iden-

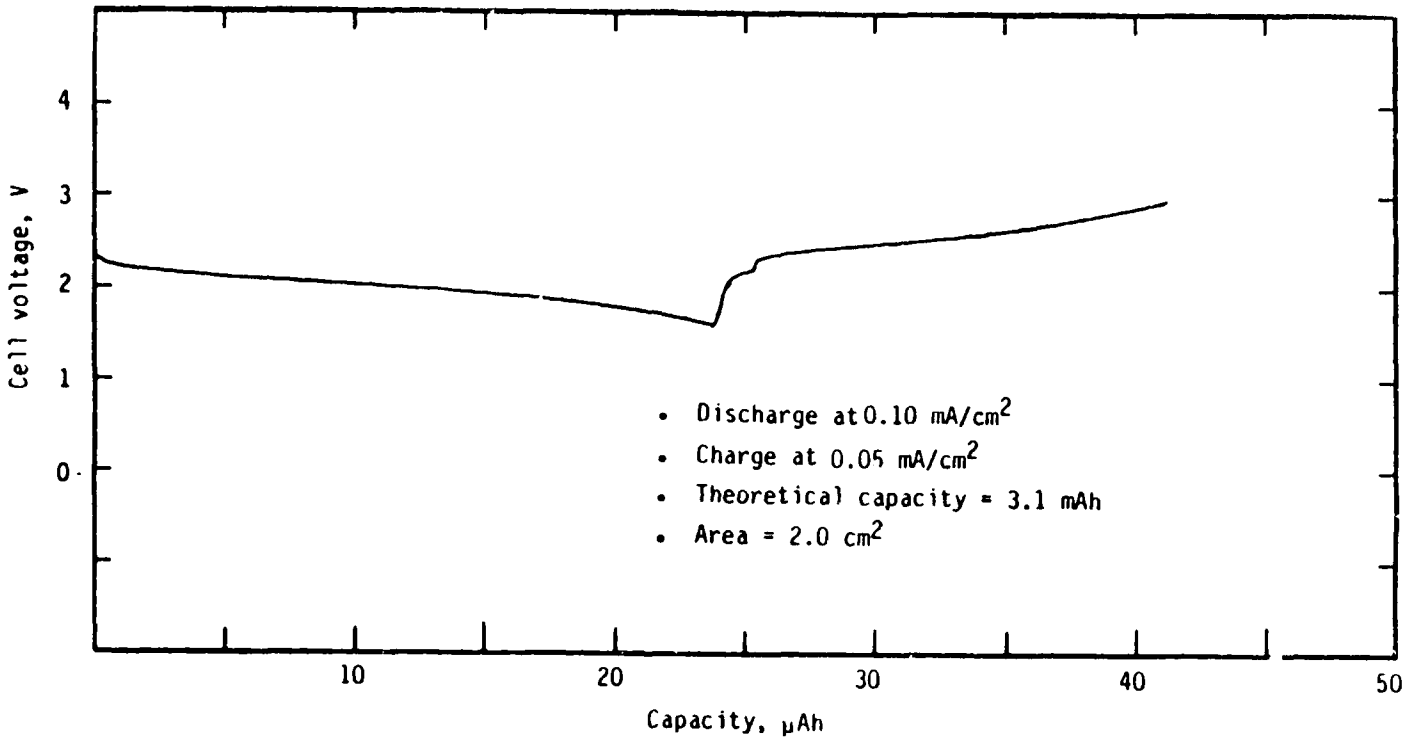

Fig. 24. Performance of $Li/PEO\text{-}LiClO_4/TiS_2$ cell at 50°C.

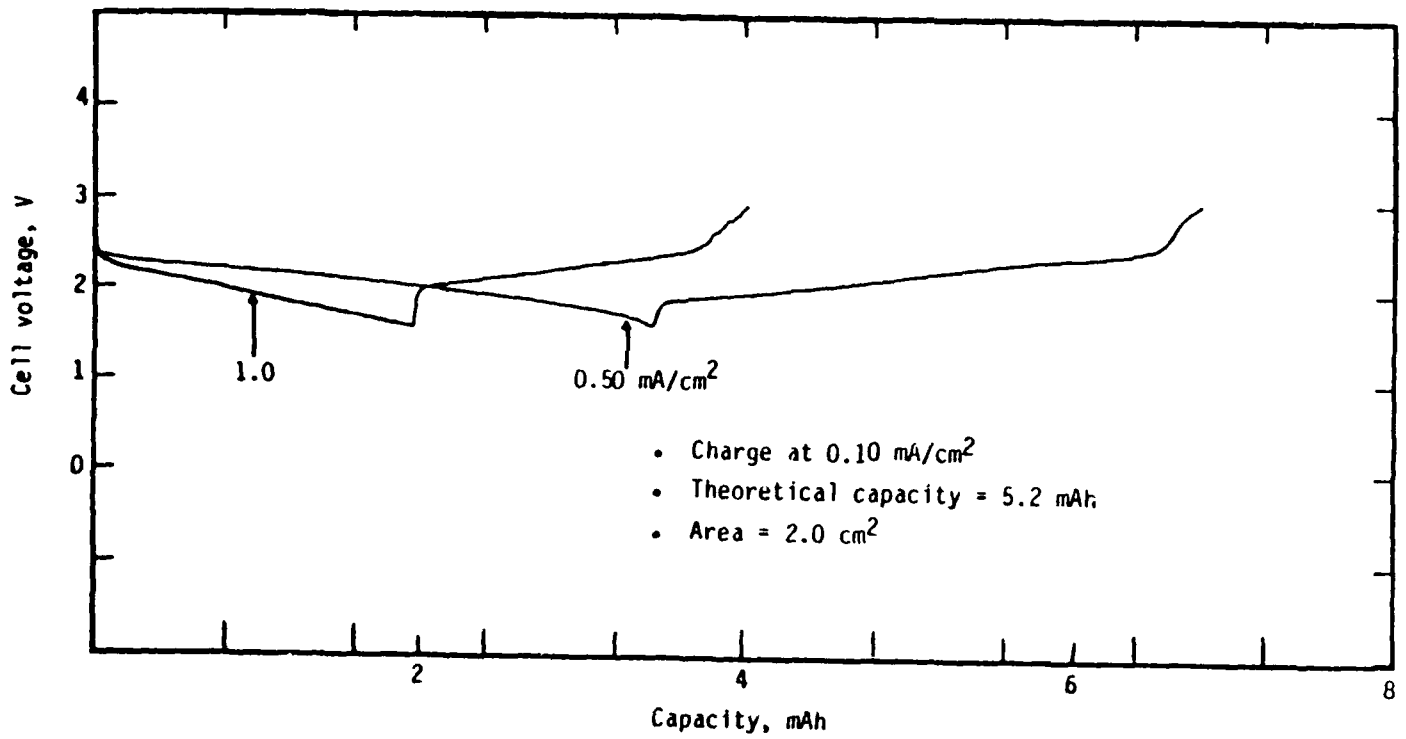

Fig. 25. Performance of $Li/PEO\text{-}LiClO_4/TiS_2$ cell at 100°C.

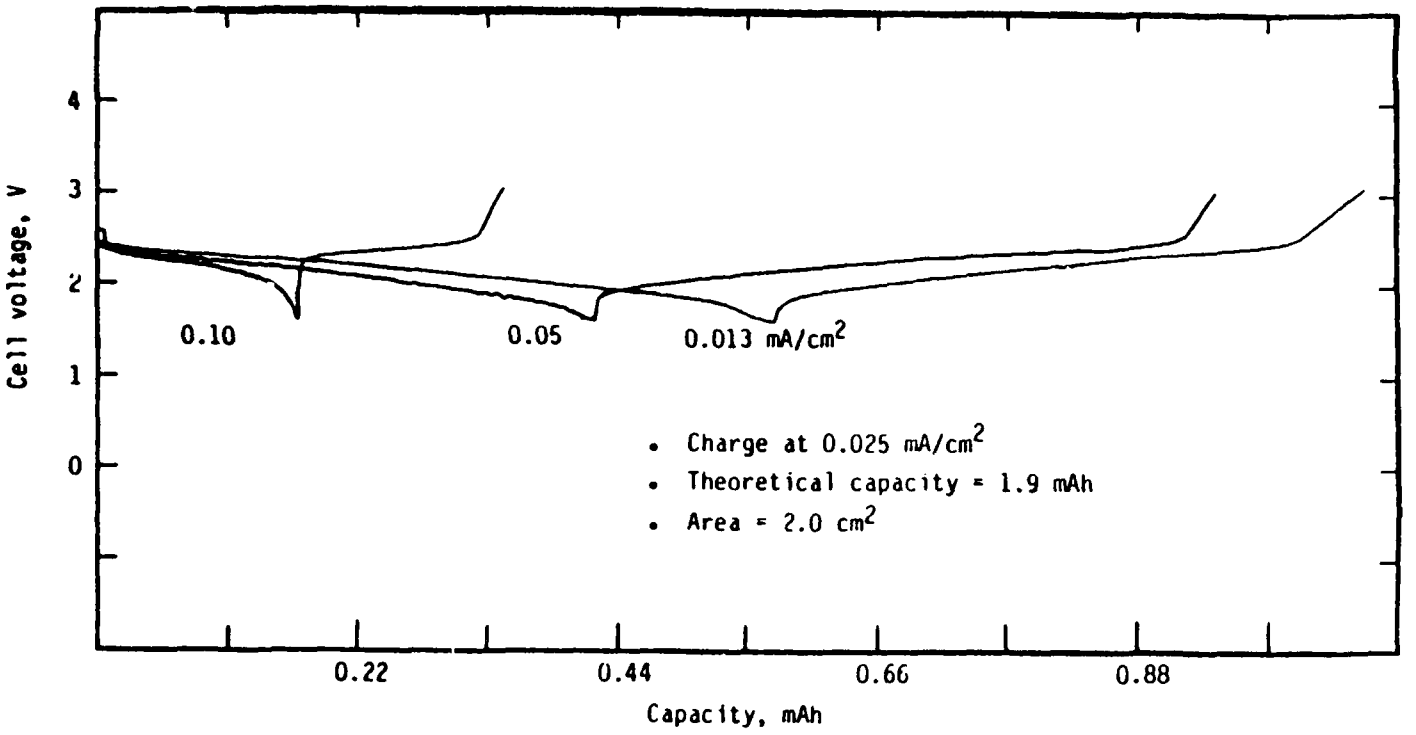

Fig. 26. Capacity-rate behavior of Li/PEO-$LiCF_3SO_3$/TiS_2 cell at 100°C.

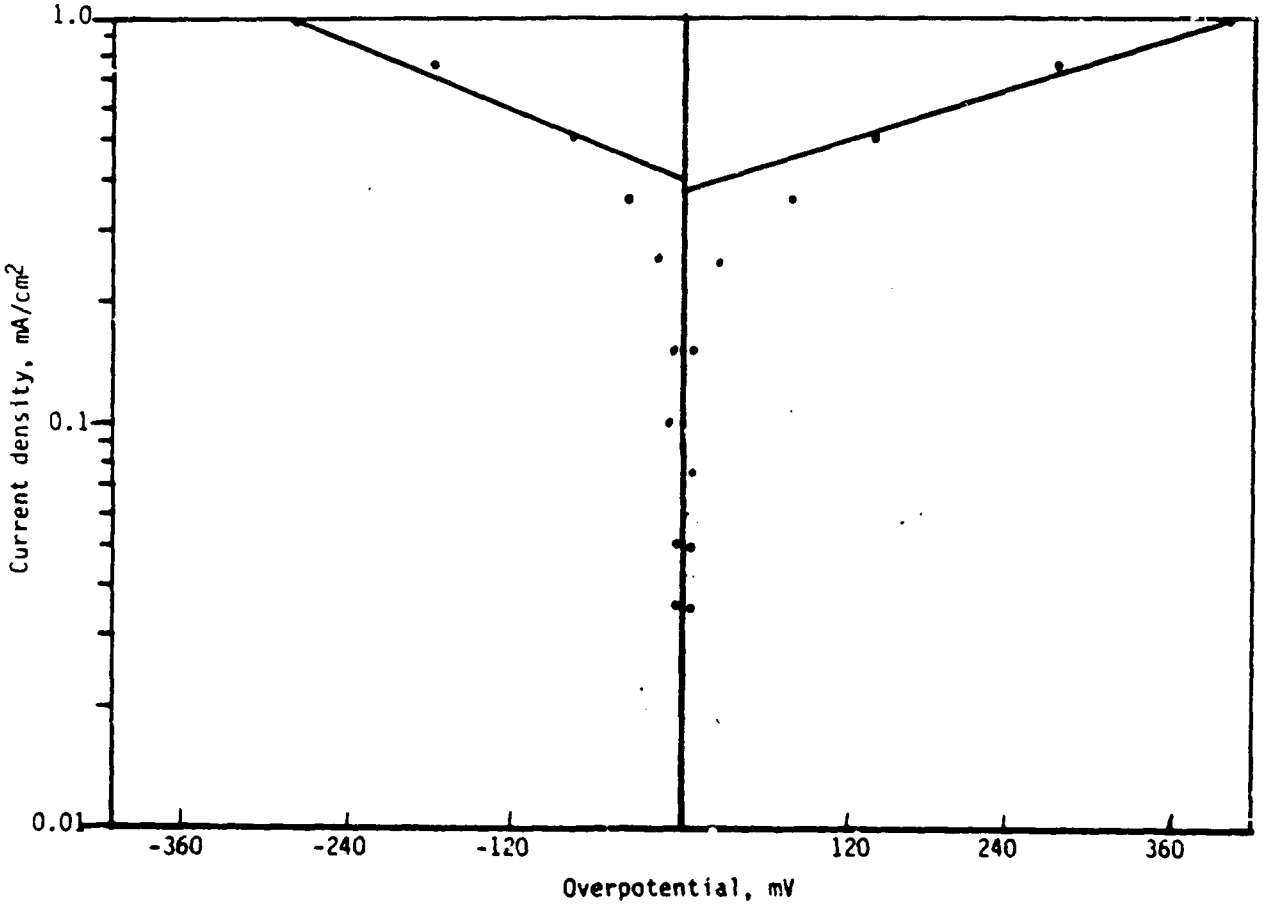

Fig. 27. Polarization behavior of the Li anode of the Li/PEO-$LiCF_3SO_3$/TiS_2 cell at 100°C.

tify the necessary conditions for its operation. Therefore, limited studies were carried out on the long-term cycling behavior of these cells.

The cycling performance of the "matrix supported" Li/MEEP/TiS_2 cells at room temperature is depicted in Figure 28. At the end of five cycles, the cell suffered approximately 10% loss in its discharge capacity. Finally, the cell failed after eight cycles due to shorting.

The cycling behavior of a Li/TiS_2 cell containing 50 w/o MEEP + 50 w/o PEO/$LiClO_4$ electrolyte at 50°C is shown in Figure 29. Again, gradual deterioration in the cell capacity was noted on cycling. There was ~12% loss in the discharge capacity at the end of the fifth cycle.

The discharge/charge behavior of a Li/TiS_2 cell with a 20 w/o MEEP + 80 w/o PEO/$LiCF_3SO_3$ electrolyte is illustrated in Figure 30. The cell was cycled 17 times and the capacity decreased from an initial utilization of 38% of the theoretical cathode capacity to 12% at the end of cycling.

The cycling performance of a cell containing PEO/$LiClO_4$ electrolyte at 100°C is shown in Figure 31. The cathode was unusually thick and that might have led to its poor utilization. At 0.50 mA/cm^2 the capacity deteriorated from the 20% initial utilization, based on theoretical cathode capacity, to 10% at the end. The cell showed a continuous degradation of performance during the course of cycling. This is clearly illustrated in Figure 32, which shows the long-term cycling performance of this cell at various current densities. The cell was cycled 64 times. At the end of this period, capacity had deteriorated from an initial 31% (at 0.20 mA/cm^2) to less than 10% of the theoretically available cathode capacity. As expected, a lowering of the discharge rate led to an increase in the cell capacity. Noteworthy is the discrepancy between the number of coloumbs on discharge and charge towards the latter part of cycling. At the end of the test, the cell was disassembled and the electrodes examined. The Li anode was found to have discolored to take on a brownish-black color. Whether the presence of residual acetonitrile, from which the electrolyte films were cast, or a reaction at the Li/electrolyte interface leads to this performance degradation remains to be investigated.

The cycling performance of a Li/PEO-$LiCF_3SO_3$/TiS_2 cell at 100°C is depicted in Figure 33. This cell had one 4.5 mil thick electrolyte. Although it delivered about 80% of the available capacity in the first cycle, the utilization dropped drastically in the subsequent cycles. At the end of five cycles, only 27% capacity could be drawn from the cell. The cell failed due to shorting at the end of 11 cycles.

2.2.6 Influence of Electrolyte Salt on Cell Performance

A comparison of the performance of cells made with electrolytes containing $LiClO_4$ and $LiCF_3SO_3$ salts shows that the latter leads to lower

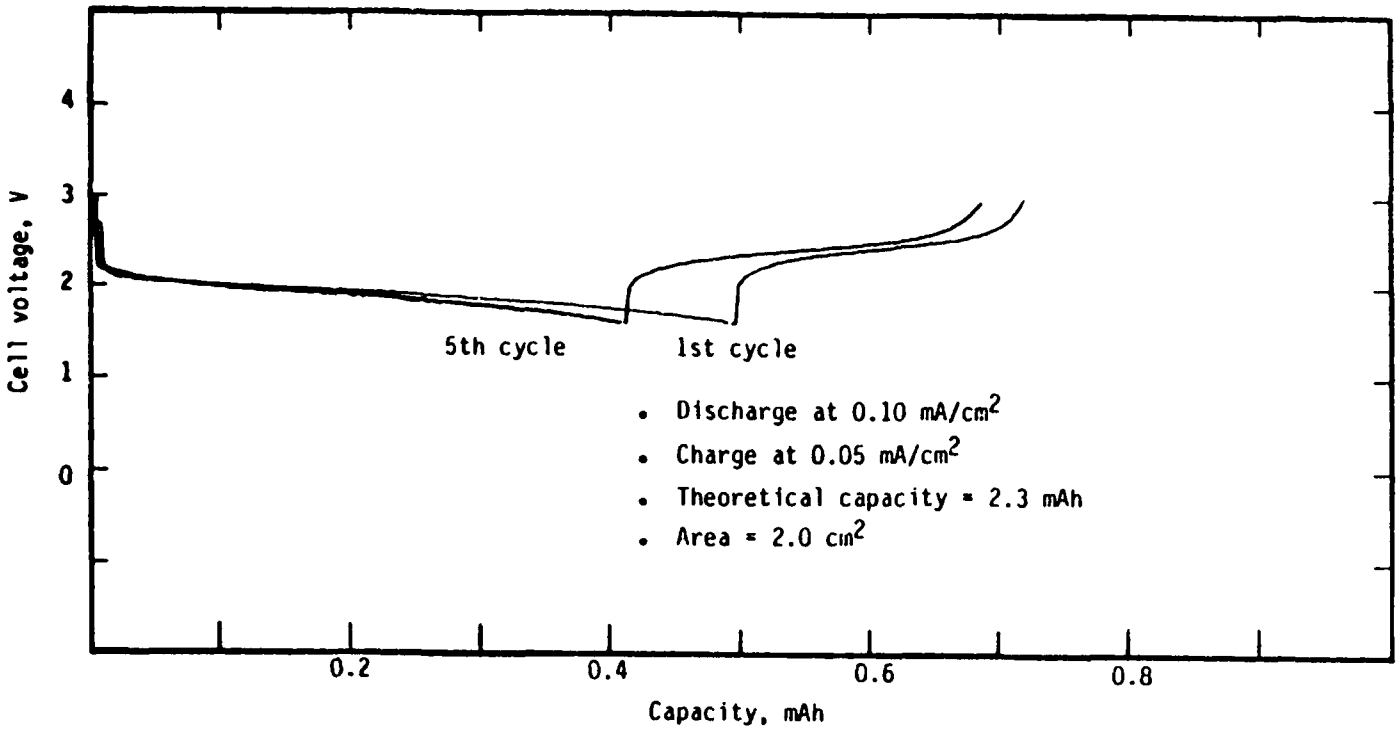

Fig. 28. Cycling performance of a "supported" Li/MEEP/TiS_2 cell.

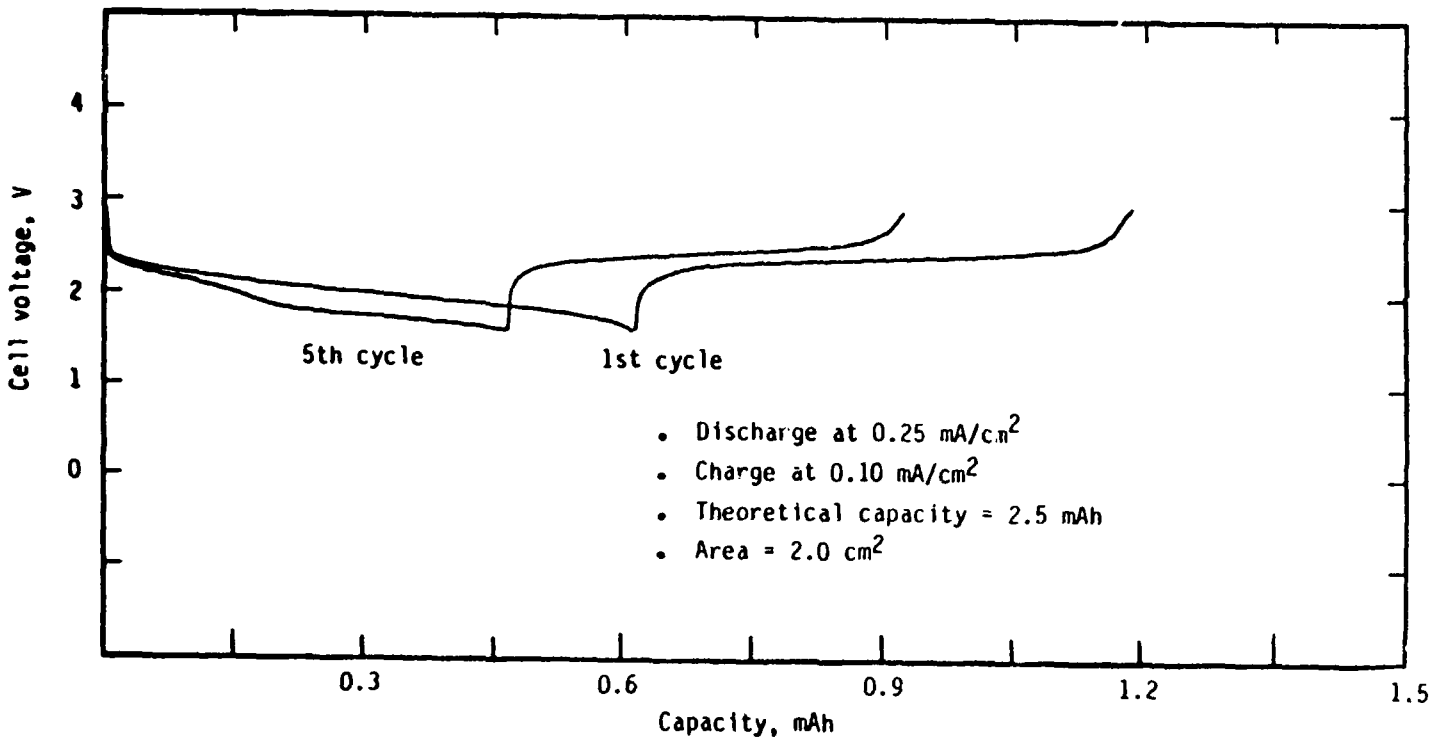

Fig. 29. Cycling performance of Li/MEEP-PEO-$LiClO_4$/TiS_2 cell at 50°C.

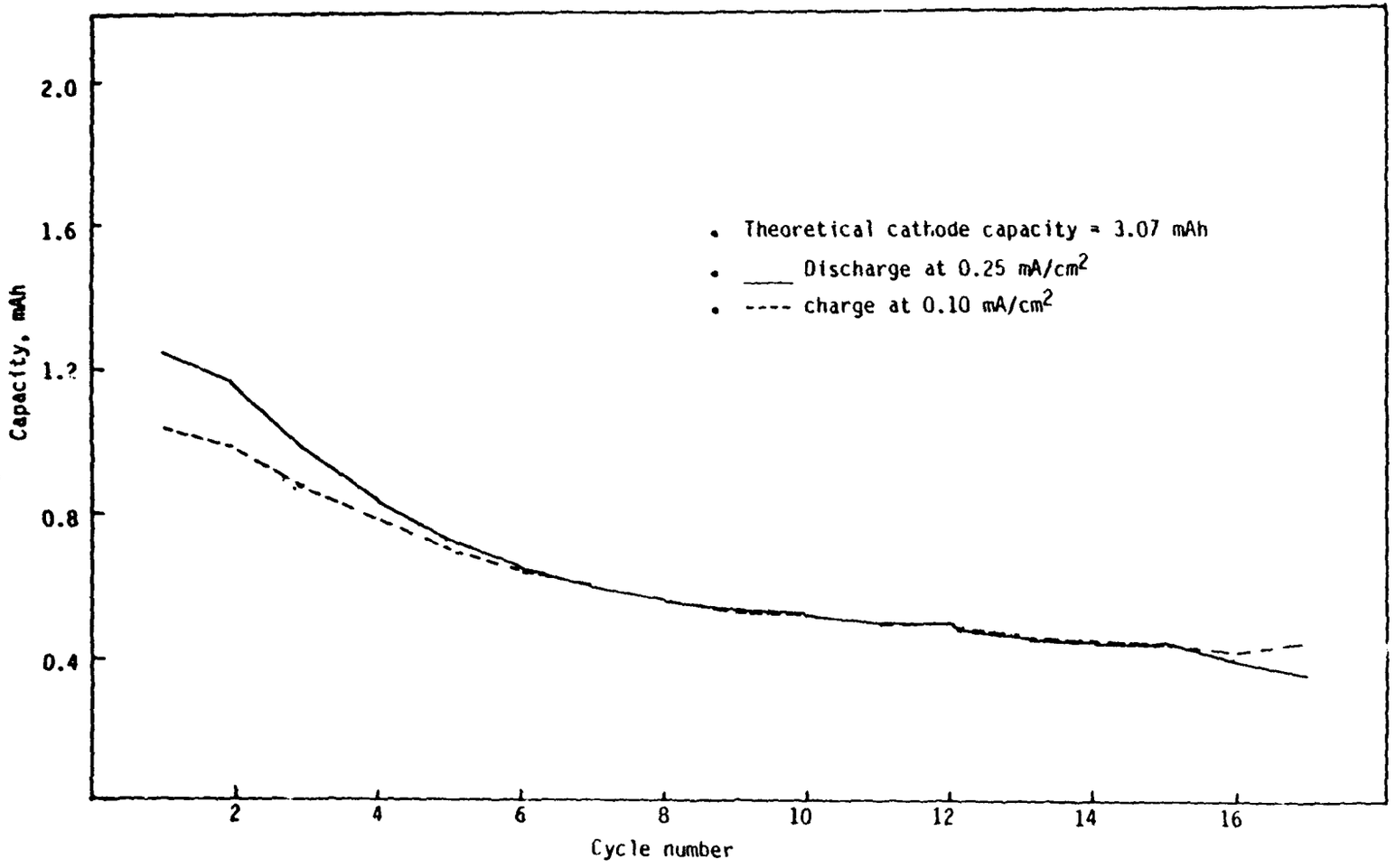

Fig. 30. Cycling performance of a Li/TiS_2 cell containing 20 w/o MEEP + 80 w/o $PEO/LiCF_3SO_3$ electrolyte at 100°C.

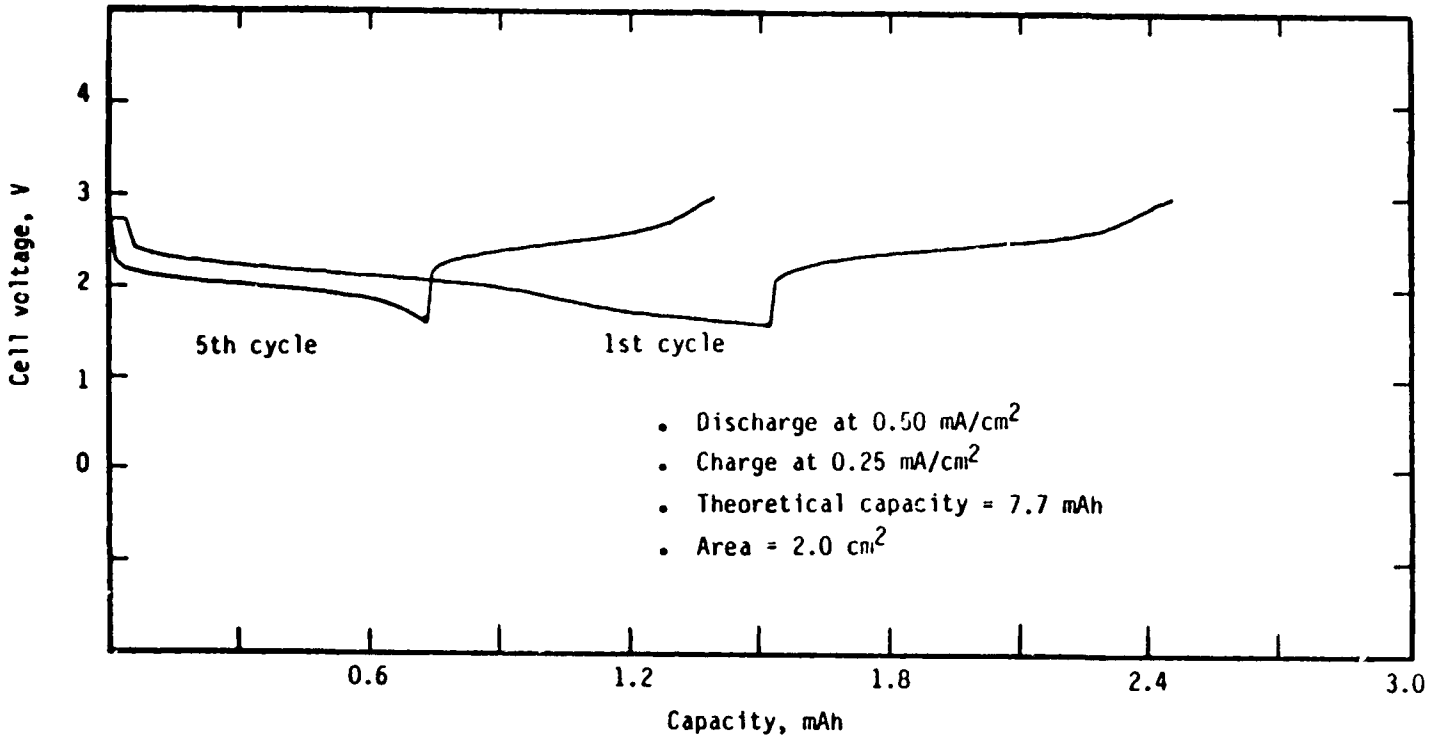

Fig. 31. Cycling performance of a Li/PEO-$LiClO_4$/TiS_2 cell at 100°C.

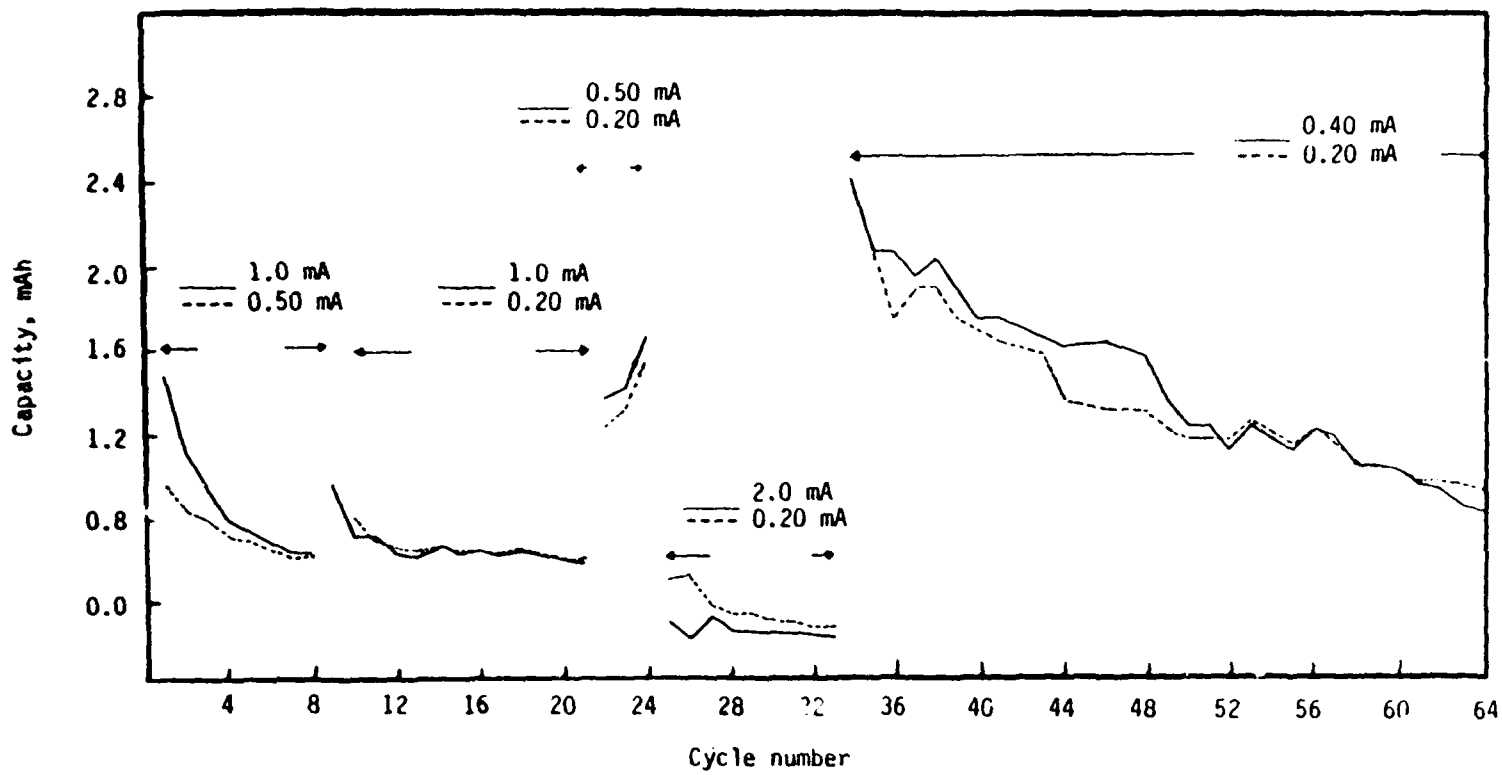

Fig. 32. Long-term cycling behavior of a Li/PEO-$LiClO_4$/TiS_2 cell at different discharge currents at 100°C.

- Theoretical cathode capacity = 7.7 mAh.
- Cathode area = 2.0 cm^2

____ discharge
---- charge

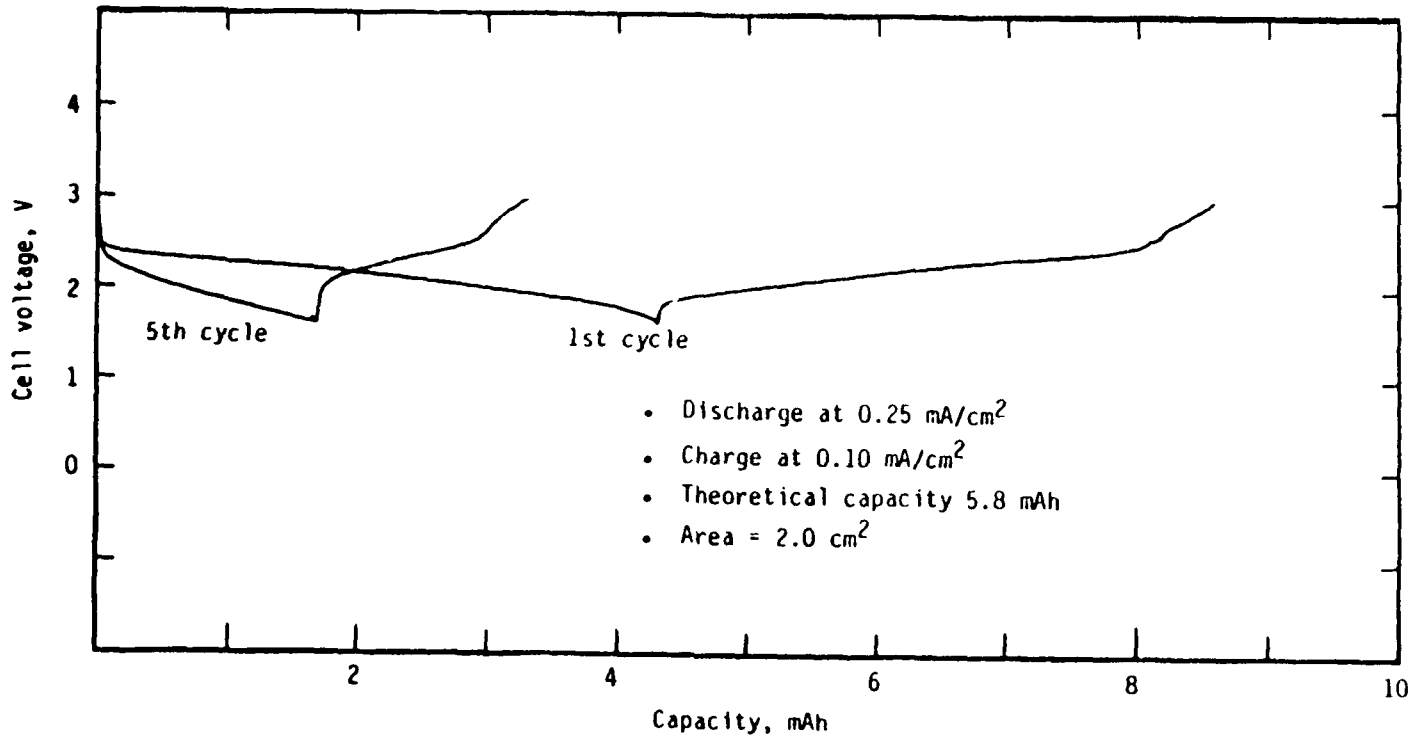

Fig. 33. Cycling performance of a $Li/PEO\text{-}LiCF_3SO_3/TiS_2$ cell at 100°C.

rate capability. We have also noticed from cycling data that cells containing $LiCF_3SO_3$ electrolytes fail, via shorting, much earlier than those containing $LiClO_4$ electrolytes. Although the reason for this is not fully understood at present, the porous structure of the $PEO/LiCF_3SO_3$ films might be an important factor. Additional studies in this regard are planned for Phase II with other salts such as $LiBF_4$, $LiPF_6$ and $LiAsF_6$.

2.3 Conclusions and Recommendations of Phase I Studies

The following important conclusions can be drawn from Phase I studies.

- Cells fabricated with MEEP electrolyte can be operated at or near room temperature at reasonable drain currents with good utilizations. A poor recharge efficiency was observed in cells cycled at room temperature.

- A major drawback of conventional MEEP electrolyte for use in an all-solid-state battery has been identified to be its poor dimensional stability, namely its tendency to flow.

- The dimensional stability of the MEEP electrolyte can be improved by supporting it on a thin, highly porous fiberglass matrix. Cells fabricated with this technique showed excellent discharge performance at room temperature.

- Improvement in the mechanical properties of MEEP electrolytes has also been achieved by mixing MEEP with PEO at 50:50 weight ratios. Thin films prepared from these mixed electrolytes have been found to be stable over a wide range of temperatures.

- The MEEP-PEO based mixed electrolytes possess significantly higher conductivities than those based on pure PEO electrolytes. At 50°C and above, the conductivities of these mixed electrolytes are similar to those of pure MEEP electrolytes.

- At and above 50°C, the performance of cells fabricated with the mixed polymer electrolytes is considerably better than those constructed with pure PEO-based electrolytes. At these temperatures, the discharge rate capabilities of MEEP-PEO and MEEP electrolyte cells were similar.

- Electrolytes prepared with $LiClO_4$ performed significantly better than those containing $LiCF_3SO_3$.

- The Li surface in contact with the electrolyte was found to undergo discoloration, most probably due to chemical reactions. The properties of the Li/electrolyte interphase remain to be studied in detail.

Recommendations for Phase II studies include:

- Optimization of the dimensional stability of MEEP-based electrolytes by incorporating poly(ethylene oxide) or poly(propylene oxide) of different molecular weights in various ratios, and using various Li salts.

- A full assessment of the scientific and technological importance of mixed electrolytes derived from MEEP and organic polymer electrolytes.

- Detailed characterization of the usefulness of fiberglass matrix supported MEEP-electrolyte in experimental cells.

- Studies of dimensionally improved MEEP electrolytes obtained by crosslinking with poly(ethylene glycol).

- Electrochemical and spectroscopic characterization of the electrode/electrolyte interfaces, determination of the electrochemical stability domain of the electrolyte and polarization behavior of the electrodes.

- Studies of alternate electrode materials, besides the Li/TiS_2 couple, such as Li-Al alloy or $Li_xFe_2O_3$ anode, and V_6O_{13} or a-V_2O_5 cathodes to improve the cycling performance of the polymer electrolyte cells.

- Fabrication and evaluation of prototype cells and bipolar series-connected batteries comprising the best anode, dimensionally stabilized MEEP electrolyte and the best cathode material.

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